Supporting Information:

Catalytic Mechanism and Efficiency of Methane Oxidation by Hg(II) in Sulfuric Acid and Comparison to Radical Initiated Conditions

Jack T. Fuller, III[‡], Steven Butler[‡], Deepa Devarajan[‡], Brian G. Hashiguchi[#], Michael M. Konnick[#], William Goddard, III,[ζ] Jason Gonzales,[ζ] Austin Jacobs[‡], Roy A. Periana[#], and Daniel H. Ess[‡]*

[‡]Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602. [#]Department of Chemistry, The Scripps Research Institute, Jupiter, Florida 33458. [ζ]Department of Chemistry, California Institute of Technology, Pasadena, California 91125, United States.

*dhe@chem.byu.edu

Table of Contents

SMD Solvated (U)M06/def2-TZVPPD//(U)M06/cc-pwCVDZ-PP[aug-cc-pVDZ] xyz coordinates and energies (hartree).

$Hg^{II}(SO_4)$
Electronic Energy = -852.6298198
Electronic and Zero-Point Energy = -852.6142058
Enthalpy = -852.6069798
Free Energy = -852.6482768

Hg	0.238828000	0.057890000	0.006366000
O	-2.354954000	1.613389000	1.510823000
O	-2.977651000	-0.784201000	1.290565000
O	-4.119177000	0.927166000	-0.130086000
O	-1.782089000	0.370748000	-0.580030000
S	-2.860477000	0.538837000	0.588482000

$Hg^{II}(HSO_4)_2$
Electronic Energy = -1552.965106
Electronic and Zero-Point Energy = -1552.909703
Enthalpy = -1552.895649
Free Energy = -1552.952952

Hg	-0.083083000	-0.128556000	-0.447710000
O	-2.768434000	1.035971000	1.303883000
O	3.129652000	0.156578000	-1.738860000
O	1.866468000	-0.622361000	0.280176000
O	4.280018000	-1.038173000	0.179330000
O	3.450574000	1.320913000	0.366000000
O	-3.419563000	-1.195276000	0.616729000
O	-4.480073000	0.761389000	-0.547325000
O	-2.123905000	0.240995000	-0.983796000
S	3.208917000	-0.143471000	-0.298766000
S	-3.223812000	0.332056000	0.093234000
H	3.647465000	1.228806000	1.315971000
H	-3.850191000	-1.735847000	-0.070767000

H_2SO_4
Electronic Energy = -700.2952964
Electronic and Zero-Point Energy = -700.2569204
Enthalpy = -700.2508694
Free Energy = -700.2851494

S	-0.000179000	0.000119000	-0.150012000
O	1.213990000	-0.332394000	0.842958000
O	0.246513000	1.253909000	-0.856247000
O	-1.211077000	0.330887000	0.847499000

O	-0.249654000	-1.252341000	-0.857674000
H	-1.527505000	-0.478363000	1.296084000
H	1.532200000	0.475968000	1.291820000

$[Hg^{II}(HSO_4)]^+$
Electronic Energy = -853.0715836
Electronic and Zero-Point Energy = -853.0442536
Enthalpy = -853.0364946
Free Energy = -853.0783796

Hg	-0.052460000	-0.169874000	-0.072896000
O	-3.037761000	0.509545000	1.470078000
O	-3.966651000	-1.315748000	0.159200000
O	-4.356935000	1.026445000	-0.633301000
O	-2.105131000	0.056877000	-0.809924000
S	-3.359454000	0.192263000	0.067095000
H	-4.370534000	-1.565506000	-0.692138000

HSO_4^-
Electronic Energy = -699.8667592
Electronic and Zero-Point Energy = -699.8404102
Enthalpy = -699.8346502
Free Energy = -699.8650292

O	0.704387000	1.352688000	-0.123035000
O	-1.487036000	0.322746000	0.070171000
O	0.306869000	-0.869466000	-1.213638000
O	0.461275000	-0.715000000	1.267760000
S	0.131246000	-0.013411000	-0.005636000
H	-1.983898000	-0.513178000	0.080121000

$[(H_2SO_4)Hg^{II}(HSO_4)]^+$
Electronic Energy = -1553.37466
Electronic and Zero-Point Energy = -1553.307811
Enthalpy = -1553.293206
Free Energy = -1553.351845

Hg	0.450453000	0.032899000	0.347848000
O	-2.946613000	1.839429000	1.381184000
O	2.279544000	2.481678000	2.002945000
O	2.551031000	0.586244000	0.377817000
O	4.536914000	1.865628000	1.030645000
O	3.371704000	0.444319000	2.742779000
O	-4.075514000	-0.313905000	1.416374000
O	-3.722543000	0.825023000	-0.797968000
O	-1.849493000	-0.206899000	0.304170000

S	3.192776000	1.452482000	1.476938000
S	-3.046171000	0.602704000	0.624723000
H	4.027690000	-0.245125000	2.531511000
H	-4.135475000	-1.215251000	1.036552000
H	-4.488495000	1.433560000	-0.742928000

$[Hg^{II}(HSO_4)_3]^-$
Electronic Energy = -2252.835523
Electronic and Zero-Point Energy = -2252.753047
Enthalpy = -2252.732141
Free Energy = -2252.806969

Hg	-0.087346000	-0.120563000	-0.305990000
O	-2.906413000	0.486404000	1.387295000
O	0.215892000	0.500558000	-3.635087000
O	1.683614000	-0.251051000	-1.757487000
O	2.443173000	-0.617273000	-4.082160000
O	2.277363000	1.715484000	-3.193721000
O	-4.009008000	-1.353566000	0.241570000
O	-4.465409000	0.979797000	-0.545829000
O	-2.250947000	-0.034616000	-0.964429000
S	1.602804000	0.226525000	-3.203101000
S	-3.391043000	0.144442000	0.034065000
H	3.241737000	1.638359000	-3.079641000
H	-4.454729000	-1.644118000	-0.574717000
O	0.417886000	0.065743000	1.943252000
S	1.819868000	0.400452000	2.439440000
O	2.863247000	0.113703000	1.431732000
O	2.028153000	-0.118929000	3.810045000
O	1.860928000	2.032443000	2.535202000
H	1.258443000	2.336764000	3.237370000

$Hg^{II}(HSO_4)_2(H_2SO_4)_2$
Electronic Energy = -2953.592801
Electronic and Zero-Point Energy = -2953.457142
Enthalpy = -2953.43112
Free Energy = -2953.517528

Hg	0.860309000	-0.415562000	-2.516649000
O	-0.591253000	-0.872546000	0.627308000
O	2.829918000	-1.758510000	-4.992341000
O	2.880423000	-0.029062000	-3.180162000
O	4.966887000	-0.580759000	-4.342175000
O	3.133782000	0.580535000	-5.592068000
O	-1.405284000	-2.819284000	-0.587832000
O	-2.984273000	-0.915293000	-0.177169000

O	-1.173543000	-0.644787000	-1.803289000
S	3.492059000	-0.546707000	-4.504170000
S	-1.554068000	-1.226954000	-0.418254000
H	3.561495000	1.425155000	-5.320696000
H	-2.010967000	-3.114523000	-1.306890000
S	-4.127676000	-1.814545000	-3.161244000
O	-3.296839000	-0.500770000	-3.507307000
O	-5.050652000	-2.037353000	-4.264925000
O	-5.018730000	-1.384067000	-1.914643000
O	-3.192452000	-2.876622000	-2.748580000
H	-4.422123000	-1.230899000	-1.134117000
H	-2.463066000	-0.464276000	-2.962789000
S	5.288494000	2.432685000	-2.918400000
O	6.436899000	1.354807000	-3.148042000
O	4.500372000	2.573425000	-4.155819000
O	4.370774000	1.782357000	-1.790875000
O	5.929318000	3.594066000	-2.318399000
H	3.756820000	1.109113000	-2.193593000
H	6.054284000	0.573011000	-3.631567000

$[Hg^{II}(HSO_4)(H_2SO_4)]^+$
Electronic Energy = -1553.386189
Electronic and Zero-Point Energy = -1553.318589
Enthalpy = -1553.304883
Free Energy = -1553.361412

Hg	1.038780000	-0.907033000	-2.258426000
O	-1.070413000	-0.283934000	0.688296000
O	-2.001257000	-2.437798000	0.037631000
O	-3.247301000	-0.355200000	-0.579076000
O	-1.157551000	-0.895320000	-1.744367000
S	-1.872491000	-0.886564000	-0.380695000
H	-2.533676000	-2.904269000	-0.645865000
S	-3.975161000	-2.153786000	-3.298502000
O	-2.823060000	-1.208801000	-3.859168000
O	-4.725279000	-2.634741000	-4.450352000
O	-4.943804000	-1.160880000	-2.519327000
O	-3.385222000	-3.108652000	-2.342679000
H	-4.469534000	-0.811158000	-1.716055000
H	-2.138315000	-1.040492000	-3.151614000

$[(HSO_4)(H_2SO_4)]^-$
Electronic Energy = -1400.187505
Electronic and Zero-Point Energy = -1400.120713
Enthalpy = -1400.109399
Free Energy = -1400.157485

O	3.335703000	0.230070000	0.185594000
O	1.708267000	-1.273909000	-0.824803000
O	1.160402000	-0.173102000	1.352800000
O	1.209813000	1.175002000	-0.734737000
S	1.875124000	0.084492000	0.057521000
H	0.749031000	-1.415549000	-0.979715000
S	-1.889036000	-0.068311000	-0.067467000
O	-1.395535000	1.401962000	-0.405357000
O	-3.346367000	-0.056266000	-0.121181000
O	-1.495018000	-0.267197000	1.459900000
O	-1.131563000	-1.030813000	-0.890486000
H	-0.492983000	-0.286906000	1.534840000
H	-0.399065000	1.397584000	-0.569828000

$[Hg^{I}(HSO_4)]^{\bullet}$
Electronic Energy = -853.2468176
Electronic and Zero-Point Energy = -853.2200526
Enthalpy = -853.2119156
Free Energy = -853.2564296

Hg	0.525763000	-0.063561000	0.164299000
O	-2.671674000	0.468568000	1.414755000
O	-3.857313000	-1.317275000	0.269212000
O	-4.301134000	1.058719000	-0.401219000
O	-2.122338000	-0.001803000	-0.981222000
S	-3.189277000	0.177475000	0.052612000
H	-4.290657000	-1.595599000	-0.556108000

CH_4
Electronic Energy = -40.49453532
Electronic and Zero-Point Energy = -40.45068932
Enthalpy = -40.44686432
Free Energy = -40.46802832

C	0.000000000	0.000000000	0.000000000
H	0.633944000	0.633944000	0.633944000
H	-0.633944000	-0.633944000	0.633944000
H	-0.633944000	0.633944000	-0.633944000
H	0.633944000	-0.633944000	-0.633944000

$[CH_4]^{\bullet+}$
Electronic Energy = -40.16650657
Electronic and Zero-Point Energy = -40.13117257
Enthalpy = -40.12630457
Free Energy = -40.15228357

C	-0.000188000	0.000661000	-0.000058000
H	0.082110000	1.059030000	0.360786000
H	1.057992000	-0.083673000	-0.362177000
H	-1.058936000	0.078466000	-0.361319000
H	-0.080035000	-1.057788000	0.363055000

$[Hg^{II}]^{+2}$
Electronic Energy = -153.1841449
Electronic and Zero-Point Energy = -153.1841449
Enthalpy = -153.1817849
Free Energy = -153.2016509

Hg 0 0 0

$[Hg^{I}]^{+}$
Electronic Energy = -153.37695
Electronic and Zero-Point Energy = -153.37695
Enthalpy = -153.37459
Free Energy = -153.395111

Hg 0 0 0

$CH_3^{\bullet}$
Electronic Energy = -39.81432999
Electronic and Zero-Point Energy = -39.78540599
Enthalpy = -39.78133299
Free Energy = -39.80422699

C	0.000000000	0.000000000	0.000056000
H	0.000000000	1.090466000	-0.000112000
H	-0.944371000	-0.545233000	-0.000112000
H	0.944371000	-0.545233000	-0.000112000

$[Hg^{II}(H_2SO_4)_2]^{2+}$
Electronic Energy = -1553.784125
Electronic and Zero-Point Energy = -1553.705777
Enthalpy = -1553.690699
Free Energy = -1553.75022

Hg	0.227462000	-0.077629000	0.580959000
O	-3.303350000	0.655519000	2.153460000
O	3.197785000	2.806448000	0.854261000
O	2.585603000	0.327969000	1.015880000
O	4.899899000	0.944362000	1.001551000
O	3.488359000	1.643530000	2.962681000

O	-4.333641000	-0.866489000	0.564145000
O	-3.849804000	1.490445000	-0.169532000
O	-2.026380000	-0.057586000	0.053193000
S	3.444816000	1.471778000	1.379002000
S	-3.284507000	0.314373000	0.740635000
H	3.569520000	0.783271000	3.422762000
H	-4.316506000	-1.248253000	-0.337731000
H	-4.661837000	1.884071000	0.211870000
H	5.571098000	1.653081000	1.084222000

$[Hg^{III}H(HSO_4)_2]^{\bullet}$
Electronic Energy = -1553.469065
Electronic and Zero-Point Energy = -1553.408969
Enthalpy = -1553.394163
Free Energy = -1553.453514

Hg	-0.281041000	0.760610000	-0.752980000
O	-3.271920000	1.053509000	1.126463000
O	2.084519000	1.459498000	-3.240454000
O	1.941638000	0.849353000	-0.817104000
O	4.151409000	0.877555000	-1.895413000
O	2.913075000	3.032922000	-1.584472000
O	-3.708135000	-0.661175000	-0.528212000
O	-4.801383000	1.586415000	-0.819823000
O	-2.391076000	1.362719000	-1.203874000
S	2.789221000	1.447858000	-1.944963000
S	-3.571898000	0.946169000	-0.311613000
H	3.489900000	3.152193000	-0.808160000
H	-3.988390000	-0.852874000	-1.442111000
H	-0.792530000	-0.476875000	0.409676000

$HSO_4^{\bullet}$
Electronic Energy = -699.5986235
Electronic and Zero-Point Energy = -699.5745705
Enthalpy = -699.5679485
Free Energy = -699.6053755

S	0.009972000	0.098524000	-0.000541000
O	-0.678030000	1.382353000	-0.002195000
O	0.974782000	-0.196615000	1.131788000
O	-1.046809000	-1.088231000	0.000934000
O	0.975773000	-0.200978000	-1.130011000
H	-1.965278000	-0.748623000	0.004526000

$(HSO_4)_2Hg^{IV}(H)(CH_3)$
Electronic Energy = -1593.2962

Electronic and Zero-Point Energy = -1593.202876
Enthalpy = -1593.18502
Free Energy = -1593.251424

Hg	-0.214429000	0.677153000	-0.923053000
O	-3.662762000	1.158094000	-0.018883000
O	2.929277000	-0.061855000	0.745333000
O	2.031727000	0.758080000	-1.446309000
O	4.431662000	0.253053000	-1.263939000
O	2.756853000	-1.616470000	-1.110504000
O	-3.849258000	-0.644242000	-1.638181000
O	-4.618197000	1.648618000	-2.311583000
O	-2.209418000	1.208656000	-2.054099000
S	3.094704000	-0.068647000	-0.720886000
S	-3.604906000	0.962513000	-1.480682000
H	2.896002000	-1.753743000	-2.065024000
H	-3.968678000	-0.868499000	-2.579071000
H	-0.565523000	-1.080747000	-0.982338000
C	-0.220508000	2.738397000	0.483611000
H	-0.889151000	2.350428000	1.256277000
H	0.854883000	2.745509000	0.680407000
H	-0.625369000	3.427230000	-0.261534000

$Hg^{II}(H)(CH_3)$
Electronic Energy = -194.005885
Electronic and Zero-Point Energy = -193.96526
Enthalpy = -193.960538
Free Energy = -193.991917

Hg	-0.294413000	0.878148000	-0.531548000
H	-0.560827000	-0.722533000	-0.076006000
C	0.035512000	2.897765000	-1.113777000
H	-0.862311000	3.511595000	-0.934947000
H	0.870572000	3.344732000	-0.550201000
H	0.278759000	2.958208000	-2.187300000

TS forming $Hg^{II}(H)(CH_3)$
Electronic Energy = -193.8726617
Electronic and Zero-Point Energy = -193.8363707
Enthalpy = -193.8310947
Free Energy = -193.8642927

Hg	-1.097021000	1.275919000	0.150243000
H	0.002313000	1.376058000	-2.490600000
C	-0.017810000	3.010771000	-1.192492000
H	-0.219810000	3.543639000	-0.259587000

H	1.044638000	2.882518000	-1.386110000
H	-0.598210000	3.387078000	-2.031887000

TS1a

Electronic Energy = -1593.4171
Electronic and Zero-Point Energy = -1593.320173
Enthalpy = -1593.303693
Free Energy = -1593.366213

Hg	0.768036000	-1.315329000	-0.482735000
O	-1.925158000	0.503791000	-0.496399000
O	2.782279000	-1.013438000	-1.200159000
O	5.105205000	-0.193990000	-1.144797000
O	3.393901000	0.840570000	0.380326000
O	4.118649000	-1.526017000	0.752719000
O	-1.304109000	2.386420000	1.043066000
O	0.326674000	1.557423000	-0.554420000
O	-1.715980000	2.800916000	-1.390984000
S	3.870071000	-0.351215000	-0.353446000
S	-1.128812000	1.808253000	-0.470345000
H	4.650399000	-1.175261000	1.490151000
H	-2.197456000	2.758729000	1.156047000
C	-1.239943000	-1.902619000	0.265821000
H	-2.092073000	-2.108806000	-0.397017000
H	-1.535633000	-1.621697000	1.283995000
H	-0.718337000	-2.874242000	0.351741000
H	-1.269631000	-0.641517000	-0.185759000

TS1b

Electronic Energy = -1593.417626
Electronic and Zero-Point Energy = -1593.321617
Enthalpy = -1593.304824
Free Energy = -1593.369074

Hg	-2.116654000	-1.395170000	1.401270000
O	-2.241650000	0.173990000	-1.260647000
O	-2.952477000	-0.818772000	3.308317000
O	-3.983859000	0.744477000	4.914264000
O	-3.889613000	1.361969000	2.477565000
O	-5.350919000	-0.527067000	3.232437000
O	-0.096092000	1.028117000	-1.961808000
O	-1.283244000	-0.614056000	-3.434254000
O	-2.172169000	1.721735000	-3.202860000
S	-3.973339000	0.303449000	3.505889000
S	-1.541576000	0.551641000	-2.559893000
H	-6.109523000	0.084703000	3.211841000

H	0.515607000	1.228711000	-2.693070000
C	-1.231365000	-2.153273000	-0.482775000
H	-0.230169000	-1.817904000	-0.781811000
H	-1.825141000	-2.564019000	-1.311223000
H	-1.070516000	-3.024745000	0.180839000
H	-1.811861000	-0.974391000	-0.683697000

$(HSO_4)Hg^{II}(CH_3)$
Electronic Energy = -893.153809
Electronic and Zero-Point Energy = -893.09147
Enthalpy = -893.0808
Free Energy = -893.130017

Hg	1.087555000	-0.055852000	0.001074000
O	-1.020669000	-0.782287000	-0.071490000
O	-1.768916000	1.524000000	-0.148535000
O	-3.198545000	-0.284823000	-1.158038000
O	-2.981926000	-0.107530000	1.324665000
S	-2.321014000	-0.010274000	0.002881000
H	-2.506974000	2.149625000	-0.034833000
C	3.060694000	0.615305000	0.063926000
H	3.728190000	-0.227399000	-0.156952000
H	3.180945000	1.406198000	-0.687884000
H	3.260900000	1.010292000	1.068300000

$[(HSO_4)Hg^{II}(CH_4)]^+$
Electronic Energy = -1593.441586
Electronic and Zero-Point Energy = -1593.339539
Enthalpy = -1593.322226
Free Energy = -1593.386599

Hg	0.312722000	-0.937822000	0.337562000
O	-0.145629000	1.019482000	-1.537756000
O	-0.492369000	-0.137517000	2.254027000
O	-1.491612000	1.581011000	3.719018000
O	-1.474371000	1.938888000	1.230010000
O	-2.897853000	0.131922000	2.221047000
O	2.108361000	1.533700000	-2.270854000
O	0.610334000	0.230354000	-3.795723000
O	0.162332000	2.654378000	-3.402177000
S	-1.515901000	0.991496000	2.365582000
S	0.561966000	1.349373000	-2.814748000
H	-3.654632000	0.736025000	2.110305000
H	2.699947000	1.685165000	-3.028416000
C	1.543294000	-2.293891000	-1.621320000
H	2.628138000	-2.279591000	-1.779812000

H	1.007677000	-2.864258000	-2.388342000
H	1.370706000	-2.807852000	-0.654351000
H	1.204096000	-1.240467000	-1.723697000

TS1c
Electronic Energy = -893.5261839
Electronic and Zero-Point Energy = -893.4578649
Enthalpy = -893.4476029
Free Energy = -893.4951909

Hg	0.868598000	-1.244495000	-0.438172000
O	-1.853501000	0.549191000	-0.543631000
O	-1.527545000	2.386731000	1.000108000
O	0.395100000	1.585081000	-0.407684000
O	-1.504995000	2.848539000	-1.458643000
S	-1.065484000	1.849447000	-0.466886000
H	-1.337906000	3.339041000	1.080752000
C	-1.165136000	-1.826802000	0.321037000
H	-2.011519000	-2.051645000	-0.344247000
H	-1.456504000	-1.506397000	1.328796000
H	-0.637630000	-2.792056000	0.431533000
H	-1.200733000	-0.586699000	-0.184170000

$[Hg^{II}(CH_3)]^+$
Electronic Energy = -193.2713563
Electronic and Zero-Point Energy = -193.2367423
Enthalpy = -193.2325023
Free Energy = -193.2631343

Hg	-0.574727000	0.213650000	0.396233000
C	0.689586000	-0.937102000	-0.817433000
H	0.159237000	-1.123518000	-1.758271000
H	0.890978000	-1.867989000	-0.274680000
H	1.605049000	-0.355311000	-0.975637000

TS1d
Electronic Energy = -1593.829715
Electronic and Zero-Point Energy = -1593.721194
Enthalpy = -1593.704302
Free Energy = -1593.768114

Hg	-2.113131000	-1.601284000	1.229654000
O	-2.534525000	-0.260033000	-1.449549000
O	-2.968100000	-0.753719000	3.179247000
O	-3.853904000	1.048232000	4.715017000
O	-3.742546000	1.485153000	2.320160000

O	-5.335893000	-0.273634000	3.149633000
O	-0.546590000	1.105513000	-1.407158000
O	-0.961045000	-0.362234000	-3.393661000
O	-2.402800000	1.658619000	-3.019413000
S	-3.907623000	0.363615000	3.436241000
S	-1.672713000	0.514811000	-2.437563000
H	-6.061645000	0.336249000	3.396984000
H	0.171889000	1.530506000	-1.910054000
C	-1.120877000	-2.361474000	-0.620164000
H	-0.162134000	-1.897890000	-0.881672000
H	-1.634541000	-2.835262000	-1.469794000
H	-0.905036000	-3.207767000	0.057568000
H	-1.899006000	-1.307636000	-0.846921000
H	-3.712876000	1.107662000	1.415402000

$[(H_2SO_4)Hg^{II}(CH_3)]^+$
Electronic Energy = -893.5709852
Electronic and Zero-Point Energy = -893.4963922
Enthalpy = -893.4856382
Free Energy = -893.5336772

Hg	0.934235000	-1.479524000	1.128598000
C	2.989434000	-1.481232000	1.500475000
H	3.281128000	-2.511236000	1.739583000
H	3.501501000	-1.123195000	0.599509000
H	3.173064000	-0.813608000	2.351340000
S	-2.266733000	-0.502632000	0.134791000
O	-2.466168000	0.812013000	1.011085000
O	-1.407252000	-1.467941000	0.849575000
O	-1.359226000	-0.021689000	-1.084865000
O	-3.600177000	-0.896008000	-0.288743000
H	-1.847291000	0.567060000	-1.697245000
H	-1.622934000	1.123935000	1.399929000

$[Hg^{II}(HSO_4)]_2^{2+}$
Electronic Energy = -1046.361867
Electronic and Zero-Point Energy = -1046.298114
Enthalpy = -1046.285869
Free Energy = -1046.339059

Hg	0.007141000	-0.460764000	-1.823941000
O	2.050779000	-3.137696000	-2.303298000
O	0.416744000	-3.565989000	-4.034563000
O	0.387255000	-4.972153000	-1.941400000
O	-0.369570000	-2.616695000	-1.848483000
S	0.623822000	-3.613430000	-2.436113000

H	-0.449090000	-3.942157000	-4.286606000
O	2.839359000	1.104072000	-3.303912000
Hg	2.864343000	-1.073150000	-2.774550000
O	0.728222000	1.607465000	-2.037333000
O	0.800812000	2.054483000	-4.411885000
O	2.188303000	3.460354000	-2.850272000
S	1.713279000	2.093766000	-3.082696000
H	1.278621000	2.429113000	-5.176882000

TS CH Activation with $[Hg^{II}(HSO_4)]_2^{2+}$

Electronic Energy = -1746.615389
Electronic and Zero-Point Energy = -1746.518285
Enthalpy = -1746.499797
Free Energy = -1746.568303

Hg	1.375769000	-0.072257000	-1.003036000
O	-1.572035000	0.931589000	-1.135815000
O	-2.893308000	1.405573000	0.828071000
O	-0.698697000	2.575162000	0.529197000
O	-2.640744000	3.168562000	-0.947286000
S	-1.881834000	2.120984000	-0.236980000
H	-3.144537000	2.041403000	1.522130000
C	-0.281613000	-0.998795000	0.145754000
H	-1.165575000	-1.507578000	-0.269478000
H	-0.445514000	-0.572479000	1.142331000
H	0.452510000	-1.822385000	0.241641000
H	-0.702813000	0.014268000	-0.596952000
Hg	3.322949000	-2.428310000	-0.970000000
O	4.604528000	-1.124517000	-2.296655000
S	4.209773000	0.213942000	-2.891072000
O	3.078241000	0.852346000	-2.118838000
O	3.496204000	-0.100092000	-4.304094000
O	5.362500000	1.091859000	-3.119598000
H	4.157767000	-0.358369000	-4.973993000

$[Hg^{II}_2(HSO_4)_3]^+$

Electronic Energy = -2406.047263
Electronic and Zero-Point Energy = -2405.963156
Enthalpy = -2405.94064
Free Energy = -2406.019664

Hg	0.132644000	-0.434761000	-0.366908000
O	-2.547883000	1.536931000	0.626649000
O	3.070848000	0.543373000	-1.598412000
O	2.139553000	-0.809956000	0.293309000
O	4.560479000	-0.921455000	-0.189638000

O	3.567707000	1.213167000	0.677599000
O	-3.548873000	-0.673254000	0.599090000
O	-4.054953000	0.876592000	-1.306782000
O	-1.817477000	-0.098607000	-1.129583000
S	3.361831000	-0.077289000	-0.270768000
S	-2.994704000	0.525908000	-0.344886000
H	3.920962000	0.948616000	1.548492000
H	-4.027935000	-1.330805000	0.061449000
Hg	1.087778000	1.385219000	-2.627006000
O	1.274374000	2.494816000	-4.534622000
S	0.263528000	2.511441000	-5.685489000
O	0.486711000	1.097211000	-6.466136000
O	-1.133491000	2.409104000	-5.223812000
O	0.610792000	3.597275000	-6.625002000
H	1.329745000	1.114029000	-6.954422000

TS CH Activation with $[Hg^{II}_2(HSO_4)_3]^+$
Electronic Energy = -2446.495559
Electronic and Zero-Point Energy = -2446.369364
Enthalpy = -2446.344371
Free Energy = -2446.429029

Hg	0.132644000	-0.434761000	-0.366908000
O	-2.547883000	1.536931000	0.626649000
O	3.070848000	0.543373000	-1.598412000
O	2.139553000	-0.809956000	0.293309000
O	4.560479000	-0.921455000	-0.189638000
O	3.567707000	1.213167000	0.677599000
O	-3.548873000	-0.673254000	0.599090000
O	-4.054953000	0.876592000	-1.306782000
O	-1.817477000	-0.098607000	-1.129583000
S	3.361831000	-0.077289000	-0.270768000
S	-2.994704000	0.525908000	-0.344886000
H	3.920962000	0.948616000	1.548492000
H	-4.027935000	-1.330805000	0.061449000
Hg	1.087778000	1.385219000	-2.627006000
O	1.274374000	2.494816000	-4.534622000
S	0.263528000	2.511441000	-5.685489000
O	0.486711000	1.097211000	-6.466136000
O	-1.133491000	2.409104000	-5.223812000
O	0.610792000	3.597275000	-6.625002000
H	1.329745000	1.114029000	-6.954422000

$[Hg^{I}(HSO_4)]_2$
Electronic Energy = -1706.578246
Electronic and Zero-Point Energy = -1706.522393

Enthalpy = -1706.506002
Free Energy = -1706.570462

Hg	0.217465000	-0.205484000	-1.719620000
O	-1.880337000	0.789409000	0.851481000
O	-2.993803000	-1.332651000	0.447164000
O	-4.110730000	0.769360000	-0.333199000
O	-2.087152000	-0.038842000	-1.501253000
S	-2.765052000	0.172780000	-0.160191000
H	-3.658890000	-1.800458000	-0.088732000
O	5.058163000	-0.538045000	-2.497403000
Hg	2.742841000	-0.425805000	-2.195374000
O	4.865743000	0.919668000	-4.520757000
O	5.824103000	-1.298629000	-4.761458000
O	7.113022000	0.425070000	-3.481394000
S	5.722642000	-0.011069000	-3.754250000
H	6.478239000	-1.932128000	-4.417677000

TS C-H activation with Hg^{I} dimer
Electronic Energy = -1747.01643
Electronic and Zero-Point Energy = -1746.91895
Enthalpy = -1746.899952
Free Energy = -1746.970555

Hg	0.468635000	-0.346925000	-1.798197000
O	-1.530824000	0.891189000	0.915813000
O	-3.036409000	-0.984745000	0.580300000
O	-3.739786000	1.283183000	-0.225563000
O	-1.935471000	0.062557000	-1.413161000
S	-2.529362000	0.434123000	-0.078775000
H	-3.743858000	-1.363171000	0.029659000
Hg	3.011743000	-0.549020000	-2.342355000
H	5.055845000	-1.862610000	-2.344459000
C	5.278150000	-0.814617000	-2.609092000
H	5.860480000	-0.889909000	-3.542173000
H	5.891352000	-0.395410000	-1.798050000
H	4.846580000	0.436404000	-3.192512000
O	4.845376000	1.525867000	-3.713214000
S	5.579580000	2.593660000	-2.883270000
O	5.394088000	3.921603000	-3.489480000
O	6.957991000	2.199176000	-2.533502000
O	4.694977000	2.515836000	-1.517581000
H	5.180244000	2.929146000	-0.780074000

(H)$Hg^{II}(HSO_4)$
Electronic Energy = -853.8555441

Electronic and Zero-Point Energy = -853.8213671
Enthalpy = -853.8129831
Free Energy = -853.8561301

Hg	0.877179000	-1.219465000	-0.402941000
O	-2.058358000	0.453584000	-0.596268000
O	-1.274572000	2.118882000	0.991838000
O	0.394201000	0.925027000	-0.429704000
O	-1.079212000	2.621313000	-1.453308000
S	-1.018316000	1.495571000	-0.495490000
H	-0.707348000	2.899561000	1.124689000
H	1.242845000	-2.794513000	-0.394937000

CH_5^+
Electronic Energy = -40.8501565
Electronic and Zero-Point Energy = -40.7984285
Enthalpy = -40.7940865
Free Energy = -40.8188815

C	0.013434000	0.017993000	0.005989000
H	0.217005000	0.946986000	0.536148000
H	1.017036000	-0.186281000	-0.576943000
H	-1.001890000	0.014497000	-0.437426000
H	0.091606000	-0.930474000	0.547790000
H	0.242044000	0.067538000	-1.155237000

Conformations of $Hg^{II}(HSO_4)_2(H_2SO_4)$:
$\Delta G = 0$
Electronic Energy = -2253.284763
Electronic and Zero-Point Energy = -2253.188601
Enthalpy = -2253.16922
Free Energy = -2253.23765

Hg	1.263325000	-0.669146000	0.639642000
O	-2.058685000	-1.033134000	1.084000000
O	2.698275000	-3.307812000	2.188437000
O	2.848870000	-0.811900000	2.097629000
O	4.294445000	-2.014888000	3.678631000
O	4.658652000	-2.316012000	1.211431000
O	-1.900694000	-2.644096000	-0.818679000
O	-2.785915000	-0.416184000	-1.252238000
O	-0.384591000	-0.656584000	-0.729765000
S	3.577280000	-2.127901000	2.400004000
S	-1.815636000	-1.095018000	-0.386656000
H	5.400388000	-1.691911000	1.324187000
H	-1.404011000	-3.191003000	-0.163201000

S	-0.611534000	-3.512225000	2.665646000
O	0.556839000	-4.123965000	3.528994000
O	-1.868249000	-3.950502000	3.266209000
O	-0.353101000	-1.958315000	2.943077000
O	-0.381009000	-3.765849000	1.228114000
H	-0.926234000	-1.434771000	2.315974000
H	1.442141000	-3.873270000	3.132068000

ΔG = 1.5
Electronic Energy = -2253.278711
Electronic and Zero-Point Energy = -2253.183059
Enthalpy = -2253.163034
Free Energy = -2253.235229

Hg	-4.727158000	-1.365204000	-1.422551000
O	-1.311904000	-0.669084000	-1.827484000
O	-7.045178000	-3.822985000	-2.299637000
O	-6.309818000	-1.490782000	-2.864296000
O	-8.179973000	-2.462430000	-4.113349000
O	-8.465234000	-1.959027000	-1.671528000
O	-1.406474000	-2.572809000	-0.203987000
O	-0.802706000	-0.270918000	0.591069000
O	-3.104637000	-0.852308000	-0.087600000
S	-7.462402000	-2.512597000	-2.826081000
S	-1.629737000	-0.990657000	-0.410169000
H	-8.894640000	-1.134734000	-1.965639000
H	-0.462649000	-2.774063000	-0.393043000
S	1.997579000	-0.990244000	-1.292274000
O	1.777061000	0.143444000	-0.196601000
O	3.422321000	-1.009191000	-1.591896000
O	1.273649000	-0.418385000	-2.589388000
O	1.309443000	-2.217680000	-0.855313000
H	0.286076000	-0.475946000	-2.464603000
H	0.861024000	0.073097000	0.191070000

ΔG = 1.6
Electronic Energy = -2253.279759
Electronic and Zero-Point Energy = -2253.18446
Enthalpy = -2253.16449
Free Energy = -2253.235122

Hg	1.248123000	-0.556735000	0.625995000
O	-2.187932000	-0.907958000	0.983354000
O	2.939337000	1.082557000	3.254463000
O	2.677251000	-1.150537000	2.124035000
O	4.207296000	-0.962151000	4.028039000

O	1.737706000	-0.690701000	4.398956000
O	-1.678385000	-2.694982000	-0.685698000
O	-2.772253000	-0.652583000	-1.450171000
O	-0.414099000	-0.530187000	-0.741368000
S	2.994628000	-0.380337000	3.420970000
S	-1.805152000	-1.104613000	-0.445527000
H	1.572245000	-1.657393000	4.451010000
H	-1.161202000	-3.098666000	0.049205000
S	-0.408738000	-3.153133000	3.002346000
O	0.658581000	-3.331897000	3.990640000
O	-1.663756000	-4.062237000	3.375961000
O	-0.912345000	-1.664027000	3.174040000
O	-0.157185000	-3.431489000	1.581454000
H	-1.411908000	-1.351261000	2.358324000
H	-1.812117000	-4.093888000	4.342519000

ΔG = 2.0
Electronic Energy = -2253.279214
Electronic and Zero-Point Energy = -2253.183472
Enthalpy = -2253.163561
Free Energy = -2253.234419

Hg	0.720393000	-0.196838000	-2.554930000
O	-0.752920000	-0.547770000	0.641368000
O	2.629829000	-1.591597000	-5.000992000
O	2.721479000	0.166421000	-3.216564000
O	4.754255000	-0.295562000	-4.508243000
O	2.780273000	0.738971000	-5.657848000
O	-1.336689000	-2.624273000	-0.483109000
O	-3.106954000	-0.871000000	-0.216895000
O	-1.287699000	-0.499051000	-1.810567000
S	3.281106000	-0.347890000	-4.557424000
S	-1.646169000	-1.048475000	-0.405371000
H	3.253311000	1.582601000	-5.535441000
H	-1.902857000	-3.022992000	-1.183099000
S	-4.056751000	-2.054025000	-3.191811000
O	-3.323785000	-0.701668000	-3.604534000
O	-4.932287000	-2.414782000	-4.297733000
O	-5.012260000	-1.623012000	-1.994118000
O	-3.049736000	-3.009233000	-2.695153000
H	-4.455918000	-1.362985000	-1.211324000
H	-2.529664000	-0.545705000	-3.022464000

ΔG = 2.4
Electronic Energy = -2253.276221
Electronic and Zero-Point Energy = -2253.180539

Enthalpy = -2253.16042
Free Energy = -2253.233774

Hg	0.718598000	-0.222933000	-2.500878000
O	-0.821211000	-0.758431000	0.661531000
O	2.714875000	-1.592209000	-4.990442000
O	2.723221000	0.121229000	-3.156711000
O	4.741106000	-0.142611000	-4.519598000
O	2.651725000	0.760909000	-5.580020000
O	-1.340363000	-2.750118000	-0.632635000
O	-3.137081000	-1.036166000	-0.277271000
O	-1.290303000	-0.537421000	-1.805258000
S	3.276397000	-0.312265000	-4.528330000
S	-1.666774000	-1.180341000	-0.462113000
H	3.015151000	1.649440000	-5.408394000
H	-1.837922000	-3.097382000	-1.410093000
S	-4.482061000	-3.136404000	-2.468264000
O	-4.553828000	-3.915437000	-1.068511000
O	-5.462814000	-3.654890000	-3.414306000
O	-4.946262000	-1.665464000	-2.107098000
O	-3.047318000	-3.153263000	-2.793013000
H	-4.298130000	-1.268573000	-1.451815000
H	-5.479121000	-4.089952000	-0.804767000

ΔG = 2.9
Electronic Energy = -2253.275313
Electronic and Zero-Point Energy = -2253.180239
Enthalpy = -2253.159725
Free Energy = -2253.233054

Hg	-0.801736000	-3.634166000	-5.087294000
O	-4.071333000	-5.015025000	-6.059133000
O	1.861455000	-2.015763000	-6.299128000
O	1.282429000	-4.159526000	-5.140079000
O	3.539216000	-3.905919000	-6.070905000
O	2.848188000	-2.484732000	-4.128501000
O	-3.706390000	-3.015831000	-7.379735000
O	-5.314007000	-2.905013000	-5.455636000
O	-2.906771000	-3.056875000	-5.006481000
S	2.385809000	-3.159441000	-5.534073000
S	-4.059209000	-3.559093000	-5.899615000
H	3.327006000	-3.137666000	-3.585164000
H	-3.710039000	-2.039971000	-7.403334000
S	-4.537717000	-0.807267000	-2.906160000
O	-3.088424000	-0.719298000	-3.574798000
O	-4.737662000	-2.158344000	-2.370981000

O	-5.529663000	-0.570594000	-4.132008000
O	-4.660785000	0.372374000	-2.056951000
H	-5.550482000	-1.389320000	-4.698873000
H	-2.907740000	-1.552398000	-4.083927000

Conformations of C-H activation transition state for $Hg(HSO_4)_2(H_2SO_4) + CH_4$:
$\Delta G^{\ddagger}$ = 32.3
Electronic Energy = -2293.737255
Electronic and Zero-Point Energy = -2293.600966
Enthalpy = -2293.578769
Free Energy = -2293.654159

Hg	-11.885615000	2.871560000	-1.772853000
O	-13.106173000	4.475359000	0.841674000
O	-10.316768000	3.565908000	-3.127437000
O	-8.235352000	4.835008000	-3.616545000
O	-8.699792000	4.035569000	-1.283967000
O	-8.214926000	2.378041000	-3.097208000
O	-10.925847000	3.767294000	1.592338000
O	-11.099303000	5.611851000	-0.077226000
O	-11.785520000	6.030937000	2.292132000
S	-8.868290000	3.823771000	-2.753875000
S	-11.756814000	5.088124000	1.162851000
H	-7.253743000	2.393326000	-2.929825000
H	-9.985488000	4.027913000	1.723795000
C	-13.419167000	2.171514000	-0.363707000
H	-14.439053000	2.574821000	-0.261027000
H	-13.058171000	1.668836000	0.540664000
H	-13.553036000	1.401894000	-1.148329000
H	-13.072843000	3.418882000	-0.011514000
S	-7.878620000	6.252520000	1.090557000
O	-9.008154000	7.140763000	0.419485000
O	-7.007653000	7.155911000	1.833496000
O	-7.017403000	5.724377000	-0.134136000
O	-8.501355000	5.106581000	1.779805000
H	-7.545977000	5.050971000	-0.655974000
H	-9.814722000	6.588202000	0.174005000

$\Delta G^{\ddagger}$ = 32.7
Electronic Energy = -2293.737068
Electronic and Zero-Point Energy = -2293.600871
Enthalpy = -2293.578413
Free Energy = -2293.653624

Hg	-11.936763000	2.976497000	-1.648215000
O	-12.801526000	4.052873000	1.046736000

O	-10.394973000	3.770496000	-2.958858000
O	-9.166864000	5.517259000	-4.166712000
O	-10.406807000	6.117278000	-2.066327000
O	-8.325937000	4.727858000	-1.985933000
O	-15.030830000	4.742438000	1.593646000
O	-14.021074000	2.842875000	2.870022000
O	-13.153359000	5.181244000	3.218521000
S	-9.646099000	5.097079000	-2.840178000
S	-13.686500000	4.161624000	2.300068000
H	-8.323110000	5.201997000	-1.119813000
H	-15.777712000	4.714856000	2.219705000
C	-13.613822000	2.080584000	-0.509130000
H	-14.597953000	2.562311000	-0.406176000
H	-13.386529000	1.369848000	0.295530000
H	-13.706468000	1.484001000	-1.434834000
H	-13.092413000	3.123736000	0.141114000
S	-9.803856000	5.653088000	1.137239000
O	-10.174858000	4.198977000	0.601036000
O	-9.942613000	5.746121000	2.586006000
O	-10.952363000	6.569377000	0.528639000
O	-8.510257000	5.952982000	0.500669000
H	-10.890653000	6.521358000	-0.464453000
H	-11.105353000	3.981197000	0.882975000

$\Delta G^{\ddagger}$ = 32.9
Electronic Energy = -2293.738549
Electronic and Zero-Point Energy = -2293.601047
Enthalpy = -2293.578902
Free Energy = -2293.653325

Hg	-11.817190000	2.866505000	-1.331667000
O	-12.735087000	3.055017000	1.575936000
O	-10.092769000	3.768793000	-2.259165000
O	-9.379285000	5.381249000	-4.002494000
O	-11.410360000	5.856843000	-2.564838000
O	-9.074362000	5.969888000	-1.666280000
O	-13.631358000	5.137247000	0.698217000
O	-14.940146000	3.901936000	2.428509000
O	-12.781895000	5.019232000	3.058502000
S	-10.073170000	5.239107000	-2.711361000
S	-13.565022000	4.257918000	2.056130000
H	-9.501248000	5.949609000	-0.780923000
H	-14.489191000	5.599633000	0.646124000
C	-13.664407000	1.888030000	-0.592772000
H	-14.572165000	2.504789000	-0.608170000
H	-13.708291000	1.084800000	0.159246000

H	-13.613932000	1.338354000	-1.548483000
H	-13.025650000	2.550363000	0.411151000
S	-9.681632000	4.597764000	1.612741000
O	-10.024341000	3.045719000	1.689012000
O	-10.079547000	5.153083000	3.045935000
O	-10.541620000	5.233796000	0.594258000
O	-8.232451000	4.698949000	1.502682000
H	-11.011169000	2.916697000	1.660851000
H	-11.073737000	5.187240000	3.131115000

$\Delta G^{\ddagger}$ = 33.0
Electronic Energy = -2293.738993
Electronic and Zero-Point Energy = -2293.601336
Enthalpy = -2293.579523
Free Energy = -2293.653036

Hg	-11.700680000	2.219521000	1.803905000
O	-11.837434000	4.121794000	-2.949584000
O	-11.659729000	2.921962000	3.866133000
O	-12.656618000	4.870375000	5.081040000
O	-14.126351000	3.304562000	3.803617000
O	-12.928325000	2.490953000	5.851236000
O	-13.957861000	3.705069000	-1.841692000
O	-11.939981000	4.172841000	-0.452759000
O	-12.980338000	6.013049000	-1.705378000
S	-12.865980000	3.498880000	4.587088000
S	-12.605551000	4.588827000	-1.786624000
H	-13.598451000	2.792596000	6.492841000
H	-14.492906000	3.910483000	-1.039794000
C	-11.709157000	1.537133000	-0.310916000
H	-10.831064000	1.687914000	-0.953741000
H	-12.653467000	1.460150000	-0.867195000
H	-11.564721000	0.550310000	0.163492000
H	-11.845484000	2.864252000	-0.180256000
S	-14.436968000	5.611099000	1.430155000
O	-12.875195000	5.475007000	1.740630000
O	-14.863291000	4.404352000	0.692245000
O	-14.748688000	6.926309000	0.876950000
O	-15.015623000	5.596512000	2.897050000
H	-12.424575000	5.028197000	0.969413000
H	-14.802959000	4.714631000	3.333728000

$\Delta G^{\ddagger}$ = 33.2
Electronic Energy = -2293.737934
Electronic and Zero-Point Energy = -2293.600874
Enthalpy = -2293.57872

Free Energy = -2293.652839

Hg	-11.471193000	2.453800000	1.957531000
O	-12.353224000	3.466340000	-2.929774000
O	-11.570834000	3.003164000	4.079074000
O	-12.534649000	3.250285000	6.336107000
O	-13.635290000	4.396416000	4.414413000
O	-13.673114000	1.890763000	4.541435000
O	-14.398079000	3.037329000	-1.690744000
O	-12.457316000	4.121234000	-0.532382000
O	-13.778512000	5.422130000	-2.153365000
S	-12.832741000	3.236813000	4.893298000
S	-13.187966000	4.096638000	-1.897141000
H	-14.548388000	1.915073000	4.970914000
H	-15.104701000	3.448242000	-1.143842000
C	-11.450484000	1.717488000	-0.139844000
H	-10.769778000	2.048260000	-0.939011000
H	-12.377224000	1.261794000	-0.511764000
H	-10.874209000	0.907083000	0.345002000
H	-11.901495000	2.974141000	-0.130111000
S	-14.953100000	4.262285000	1.478657000
O	-13.767666000	5.331517000	1.466440000
O	-14.403597000	2.910349000	1.635246000
O	-15.849712000	4.500043000	0.336249000
O	-15.708802000	4.739622000	2.779257000
H	-13.122556000	5.056666000	0.759307000
H	-15.094298000	4.600327000	3.556954000

$\Delta G^{\ddagger}$ = 33.7
Electronic Energy = -2293.734487
Electronic and Zero-Point Energy = -2293.597656
Enthalpy = -2293.575115
Free Energy = -2293.651929

Hg	-10.359722000	1.945308000	0.331399000
O	-12.784797000	3.689989000	-0.438194000
O	-8.250122000	2.447940000	0.288014000
O	-6.285774000	3.927790000	0.130058000
O	-8.497867000	4.714015000	-0.768403000
O	-8.195353000	4.403506000	1.702627000
O	-14.554700000	5.347409000	-0.915104000
O	-14.333993000	4.340792000	1.395739000
O	-15.179659000	2.963014000	-0.395170000
S	-7.758726000	3.894058000	0.214785000
S	-14.197673000	4.198233000	-0.074059000
H	-8.094976000	5.370560000	1.773817000

H	-15.330411000	2.880768000	-1.356220000
C	-12.459046000	1.322984000	0.691938000
H	-13.115060000	0.961184000	-0.111523000
H	-13.000648000	1.732178000	1.556107000
H	-11.954785000	0.413096000	1.066633000
H	-12.415820000	2.540486000	0.088703000
S	-11.215090000	5.372894000	2.282425000
O	-12.621600000	6.024947000	2.653833000
O	-10.212396000	6.240816000	2.891441000
O	-11.098181000	5.605129000	0.703411000
O	-11.252357000	3.931477000	2.553989000
H	-11.535914000	4.868540000	0.206152000
H	-13.359164000	5.460730000	2.295199000

CH_3^+
Electronic Energy = -39.59169828
Electronic and Zero-Point Energy = -39.56085228
Enthalpy = -39.55704728
Free Energy = -39.57995228

C	-2.706045000	-0.207265000	0.048199000
H	-2.728700000	-0.195491000	-1.049196000
H	-2.707946000	-1.164033000	0.585656000
H	-2.680691000	0.735374000	0.609469000

Hg^0
Electronic Energy = -153.5594087
Electronic and Zero-Point Energy = -153.5594087
Enthalpy = -153.5570487
Free Energy = -153.5769147

Hg 0 0 0

TS front-side S_N2 forming CH_3OSO_3H + Hg^0
Electronic Energy = -893.0701191
Electronic and Zero-Point Energy = -893.0078131
Enthalpy = -892.9980171
Free Energy = -893.0444921

Hg	-2.961551000	6.240927000	-1.032224000
O	-6.534669000	3.306560000	0.449818000
O	-5.583820000	4.037537000	-1.753711000
O	-4.091357000	3.696931000	0.218688000
O	-5.165216000	1.761137000	-0.971616000
S	-5.343157000	3.122069000	-0.412887000
H	-5.206896000	4.928084000	-1.602696000

C	-2.304021000	3.401867000	-1.162183000
H	-2.456768000	2.490192000	-0.591556000
H	-2.757680000	3.500301000	-2.148957000
H	-1.436453000	4.016123000	-0.922963000

TS2

Electronic Energy = -893.1076538
Electronic and Zero-Point Energy = -893.0444888
Enthalpy = -893.0346758
Free Energy = -893.0816408

Hg	-0.154026000	-0.226601000	-0.010885000
C	-2.752709000	-0.206163000	0.047060000
H	-2.713124000	-0.197373000	-1.039473000
H	-2.692288000	-1.151631000	0.580290000
H	-2.665261000	0.723751000	0.606252000
S	-5.407907000	1.022102000	-0.243764000
O	-4.705636000	-0.285046000	0.117789000
O	-4.790680000	1.711188000	-1.393908000
O	-5.065844000	2.036569000	0.991733000
O	-6.873602000	0.828047000	-0.267147000
H	-5.507410000	1.726247000	1.802796000

$[(HSO_4)HgHg(CH_3)]^{+2}$

Electronic Energy = -1046.361867
Electronic and Zero-Point Energy = -1046.298114
Enthalpy = -1046.285869
Free Energy = -1046.339059

Hg	1.207547000	-0.031789000	-1.123832000
C	-0.040085000	-1.170883000	0.126761000
H	-1.051105000	-0.840621000	-0.143688000
H	0.219964000	-0.911821000	1.159287000
H	0.092902000	-2.240879000	-0.067820000
Hg	3.047442000	-2.218482000	-0.714725000
O	4.473915000	-0.951378000	-2.086108000
S	4.116314000	0.279161000	-2.889734000
O	2.884008000	0.965746000	-2.367764000
O	3.592158000	-0.252319000	-4.332412000
O	5.269305000	1.165122000	-3.118320000
H	4.340413000	-0.574212000	-4.868525000

TS MR Functionalization of $[(HSO_4)HgHg(CH_3)]^{+2}$

Electronic Energy = -1746.225226
Electronic and Zero-Point Energy = -1746.134104
Enthalpy = -1746.115586

Free Energy = -1746.185059

Hg	-0.939037000	-0.463610000	0.142009000
O	-3.249507000	1.994263000	0.914293000
O	-4.040229000	0.349028000	2.516369000
O	-5.360128000	0.688336000	0.414623000
O	-3.170365000	-0.430949000	0.294600000
S	-3.972486000	0.707716000	0.924799000
H	-4.620615000	-0.420613000	2.658427000
Hg	1.591766000	0.182665000	-0.524640000
H	1.509441000	-2.376495000	0.670866000
C	1.976909000	-1.533672000	1.175952000
H	3.014953000	-1.275245000	0.953343000
H	1.480738000	-1.061635000	2.020771000
O	2.809304000	-2.997187000	2.691845000
S	4.069664000	-3.636220000	2.165608000
O	5.032307000	-2.665638000	1.593880000
O	3.602380000	-4.465971000	0.825547000
H	3.019515000	-5.200442000	1.086946000
O	4.628596000	-4.632378000	3.112344000

$[(HSO_4)_2HgHg(CH_3)]^+$
Electronic Energy = -1746.246816
Electronic and Zero-Point Energy = -1746.154797
Enthalpy = -1746.136276
Free Energy = -1746.204594

Hg	-0.933622000	-0.841755000	0.582954000
O	-3.088253000	-3.227436000	1.925981000
O	-4.231067000	-2.730120000	-0.155478000
O	-5.178826000	-1.797184000	1.969744000
O	-3.085680000	-0.869958000	1.080004000
S	-3.894860000	-2.146999000	1.328885000
H	-4.865440000	-2.144737000	-0.607857000
Hg	1.595480000	0.286938000	-0.193789000
H	1.532749000	-2.093830000	1.125431000
C	2.317965000	-1.366894000	0.886539000
H	3.061805000	-1.804196000	0.208340000
H	2.762939000	-0.948839000	1.797049000
O	0.740029000	1.985082000	-1.401131000
S	-0.689201000	1.983957000	-1.922862000
O	-0.613446000	1.282606000	-3.392252000
H	-0.149009000	1.870115000	-4.015913000
O	-1.186822000	3.360893000	-2.114524000
O	-1.573150000	1.048731000	-1.176735000

TS MR Functionalization of $[(HSO_4)_2HgHg(CH_3)]^+$
Electronic Energy = -2446.102085
Electronic and Zero-Point Energy = -2445.983396
Enthalpy = -2445.958288
Free Energy = -2446.043889

Hg	-0.781244000	-0.401292000	-0.025581000
O	-3.241228000	2.102366000	0.412251000
O	-3.385306000	0.697880000	2.385210000
O	-5.243263000	0.586745000	0.697942000
O	-3.042018000	-0.380804000	0.149484000
S	-3.781551000	0.784375000	0.800326000
H	-3.766341000	-0.109595000	2.775389000
Hg	1.709890000	0.305905000	-0.763991000
H	1.337381000	-2.438174000	0.392804000
C	1.630794000	-1.621729000	1.048484000
H	2.635874000	-1.199437000	0.987642000
H	0.989765000	-1.309169000	1.870773000
O	2.487720000	-3.170166000	2.452714000
S	3.874407000	-3.580455000	2.024928000
O	4.785816000	-2.435566000	1.793496000
O	3.696144000	-4.172168000	0.501118000
H	3.158723000	-4.983046000	0.526923000
O	4.409527000	-4.687564000	2.855257000
O	2.911560000	1.857452000	-2.000189000
S	2.718204000	3.352962000	-1.806441000
O	1.157192000	3.636192000	-2.215307000
H	1.049813000	3.554194000	-3.179469000
O	3.564158000	4.118828000	-2.749714000
O	2.746693000	3.765087000	-0.386902000

TS Concerted Protonation-Deprotonation of Methane
Electronic Energy = -740.7310516
Electronic and Zero-Point Energy = -740.6516786
Enthalpy = -740.6429426
Free Energy = -740.6840276

C	-1.922702000	-2.262609000	0.332557000
H	-1.051670000	-2.877944000	0.590118000
H	-1.864317000	-1.291655000	-0.371049000
H	-2.693729000	-2.183771000	1.098061000
H	-2.307852000	-2.711212000	-0.598475000
S	-0.740631000	0.996825000	-0.495417000
O	-0.317914000	0.184899000	0.697627000
O	-1.069187000	2.403970000	-0.185887000
O	0.536169000	1.026095000	-1.512157000

O	-1.756986000	0.240184000	-1.293043000
H	1.176082000	1.698232000	-1.216646000
H	-1.238168000	-1.280390000	0.463891000

CH_3OSO_3H
Electronic Energy = -739.5744067
Electronic and Zero-Point Energy = -739.5082287
Enthalpy = -739.5006567
Free Energy = -739.5385787

S	0.465358000	-0.110238000	0.051614000
O	-0.906280000	-0.333049000	-0.746062000
O	0.337293000	-0.548970000	1.439582000
O	0.573544000	1.489093000	0.149868000
O	1.502125000	-0.636167000	-0.833267000
H	0.763352000	1.879880000	-0.725709000
C	-2.122742000	0.012523000	-0.036575000
H	-2.065838000	1.042841000	0.337884000
H	-2.913360000	-0.067451000	-0.788401000
H	-2.297166000	-0.698407000	0.779222000

$Hg^{II}(CF_3SO_3)_2$
Electronic Energy = -2076.606534
Electronic and Zero-Point Energy = -2076.550579
Enthalpy = -2076.531378
Free Energy = -2076.602733

Hg	-0.064444000	-0.124391000	0.258330000
O	-3.251335000	0.077479000	1.587047000
O	2.561896000	0.447362000	-1.626019000
O	1.980936000	0.258654000	0.812587000
O	4.119476000	1.356848000	0.170514000
O	-4.372223000	-1.362260000	-0.186967000
O	-2.013096000	-0.652051000	-0.480088000
S	3.089800000	0.388188000	-0.247061000
S	-3.367907000	-0.345949000	0.176571000
C	3.919333000	-1.272788000	-0.121748000
F	4.920885000	-1.318377000	-0.989995000
F	4.388291000	-1.448876000	1.105028000
F	3.042731000	-2.227587000	-0.405708000
C	-3.884120000	1.185878000	-0.746286000
F	-2.996446000	2.150228000	-0.537711000
F	-3.956055000	0.922501000	-2.043566000
F	-5.073232000	1.576852000	-0.307440000

$[Hg^{I}(CF_3SO_3)]_2$

Electronic Energy = -2230.224522
Electronic and Zero-Point Energy = -2230.168526
Enthalpy = -2230.146751
Free Energy = -2230.226212

Hg	-1.167428000	0.962065000	-1.471818000
O	-3.834797000	-1.408781000	-1.742095000
O	3.388512000	-1.756658000	-0.049610000
O	3.741711000	0.407061000	-1.279233000
O	5.707677000	-1.052248000	-0.779463000
O	-5.803947000	0.152458000	-2.043422000
O	-3.522624000	1.084948000	-1.625478000
S	4.333755000	-0.664231000	-0.386320000
S	-4.462182000	-0.093480000	-1.465779000
C	4.560076000	0.241684000	1.223848000
F	5.108558000	-0.571693000	2.120398000
F	5.352593000	1.293852000	1.048522000
F	3.379983000	0.656461000	1.676773000
C	-4.755805000	-0.110303000	0.372149000
F	-3.606724000	-0.315273000	1.011022000
F	-5.267085000	1.053292000	0.760265000
F	-5.604666000	-1.084961000	0.681284000
Hg	1.422822000	0.772963000	-1.426986000

$CH_3OSO_2CF_3$
Electronic Energy = -1001.388584
Electronic and Zero-Point Energy = -1001.322539
Enthalpy = -1001.312118
Free Energy = -1001.358864

C	-3.040411000	-0.319167000	-0.035952000
H	-2.902745000	-0.450183000	-1.114254000
H	-2.726025000	-1.219181000	0.499973000
H	-2.491971000	0.553017000	0.336633000
S	-5.258619000	1.059003000	-0.297664000
O	-4.460432000	-0.205182000	0.272029000
O	-4.545686000	1.693742000	-1.409575000
O	-6.666930000	0.672164000	-0.378715000
C	-5.133918000	2.225683000	1.156884000
F	-5.828963000	3.311468000	0.863839000
F	-5.636120000	1.639026000	2.227121000
F	-3.866356000	2.539484000	1.360428000

CF_3SO_3H
Electronic Energy = -962.1108847
Electronic and Zero-Point Energy = -962.0724907

Enthalpy = -962.0638197
Free Energy = -962.1052717

O	-2.760902000	0.901869000	1.339243000
O	-3.712717000	-1.185853000	0.453705000
O	-2.115068000	0.199815000	-1.004959000
S	-3.159571000	0.092933000	0.015680000
H	-2.098651000	1.597926000	1.149195000
C	-4.597406000	1.132133000	-0.569946000
F	-4.179169000	2.369356000	-0.767292000
F	-5.040930000	0.615489000	-1.701649000
F	-5.545374000	1.107850000	0.347162000

TS forming $[Hg^{II}(HSO_3)]^+ + H_2O$ from H_2SO_4
Electronic Energy = -854.2267619
Electronic and Zero-Point Energy = -854.1771639
Enthalpy = -854.1686589
Free Energy = -854.2115939

S	-1.756634000	-0.432960000	0.442746000
O	-1.417043000	1.475429000	0.025567000
O	-3.146442000	-0.311533000	-0.276959000
O	-1.713194000	-0.192688000	1.872225000
O	-0.768669000	-0.995061000	-0.453676000
H	-0.661433000	1.834973000	0.530519000
H	-1.233116000	1.649026000	-0.918761000
H	-3.840222000	0.063206000	0.313240000
Hg	-2.551665000	-3.301445000	1.149059000

TS forming $Hg^{II}SO_3 + H_2O$ from H_2SO_4
Electronic Energy = -853.84023
Electronic and Zero-Point Energy = -853.803954
Enthalpy = -853.794656
Free Energy = -853.840355

S	-1.956160000	-0.665432000	0.462324000
O	-1.433799000	1.532269000	-0.207021000
O	-3.357352000	-0.448598000	0.116171000
O	-1.498520000	-0.418996000	1.827168000
O	-1.028276000	-1.186363000	-0.537528000
H	-1.388638000	2.136924000	0.548216000
H	-0.547402000	1.557949000	-0.596144000
Hg	-2.649388000	-3.651499000	1.253977000

SO_3
Electronic Energy = -623.8129747

Electronic and Zero-Point Energy = -623.8011627
Enthalpy = -623.7966007
Free Energy = -623.8276567

S	-0.070767000	0.193376000	0.102474000
O	0.268936000	-1.221542000	0.107493000
O	0.980420000	1.194626000	0.004831000
O	-1.462462000	0.607560000	0.197070000

H_2O
Electronic Energy = -76.43820513
Electronic and Zero-Point Energy = -76.41699213
Enthalpy = -76.41321213
Free Energy = -76.43464813

O	2.550177000	0.038100000	0.513113000
H	2.814344000	0.952378000	0.673389000
H	2.647003000	-0.388632000	1.373220000

$(H_2SO_4)_3$
Electronic Energy = -2100.912147
Electronic and Zero-Point Energy = -2100.794242
Enthalpy = -2100.775355
Free Energy = -2100.84316

O	3.451553000	-0.350176000	-0.123270000
O	1.228539000	-1.270080000	-0.870333000
O	1.347983000	-0.125476000	1.265535000
O	1.731374000	1.188974000	-0.855733000
S	1.998415000	-0.151813000	-0.047685000
H	1.644283000	-1.356518000	-1.765801000
S	-1.500996000	1.406989000	0.895678000
O	-0.967500000	1.169642000	-0.454824000
O	-0.446982000	2.421664000	1.542858000
O	-1.357060000	0.091666000	1.777668000
O	-2.871119000	1.863932000	1.082006000
H	-0.440680000	-0.268942000	1.681212000
H	0.760544000	1.395245000	-0.845022000
H	-0.750530000	2.751722000	2.412276000
O	4.708891000	-0.501007000	-4.642895000
S	4.138734000	-0.707080000	-3.318152000
O	4.733564000	0.453088000	-2.406302000
O	4.698291000	-2.044936000	-2.643568000
H	5.655482000	-2.156663000	-2.813164000
H	4.380042000	0.364710000	-1.484331000
O	2.683561000	-0.804222000	-3.141743000

$(SO_3)(H_2SO_4)$
Electronic Energy = -1324.120352
Electronic and Zero-Point Energy = -1324.069031
Enthalpy = -1324.057997
Free Energy = -1324.105543

O	0.316873000	1.333742000	-0.944239000
O	-1.153914000	-0.262743000	0.171553000
O	0.955867000	-1.102713000	-0.937917000
O	0.974815000	0.171180000	1.212315000
S	0.337150000	0.058718000	-0.248763000
H	-1.239561000	-1.162034000	0.557743000
H	1.953076000	0.219740000	1.178940000
O	2.415168000	-2.623933000	0.989718000
S	1.245130000	-3.111719000	0.275860000
O	-0.071578000	-2.992730000	0.896530000
O	1.399939000	-3.886152000	-0.944044000

$(H_2O)(H_2SO_4)$
Electronic Energy = -776.747064
Electronic and Zero-Point Energy = -776.685216
Enthalpy = -776.676078
Free Energy = -776.71826

O	0.729628000	0.934625000	1.202281000
O	-0.988009000	-0.330243000	-0.122772000
O	0.071165000	1.580182000	-1.175464000
O	1.457485000	-0.444376000	-0.671364000
S	0.354144000	0.561338000	-0.162745000
H	-0.963642000	-0.956768000	0.626095000
O	1.239700000	-0.796399000	-3.199116000
H	1.240481000	0.036141000	-3.690826000
H	1.367690000	-0.602222000	-1.682609000
H	0.427560000	-1.247914000	-3.466360000

HSO_3^+
Electronic Energy = -624.1657133
Electronic and Zero-Point Energy = -624.1429243
Enthalpy = -624.1379383
Free Energy = -624.1697213

O	3.519473000	-0.133284000	0.806585000
O	2.239006000	-2.376361000	1.152826000
O	2.355834000	-0.552375000	2.921442000
S	2.719925000	-1.077709000	1.527344000

H	1.795171000	-1.166912000	3.471629000

$Hg^{II}SO_3$
Electronic Energy = -777.4090616
Electronic and Zero-Point Energy = -777.3974156
Enthalpy = -777.3909606
Free Energy = -777.4295006

Hg	-0.248008000	0.143639000	-0.757394000
O	-2.161183000	1.609638000	1.396166000
O	-2.748221000	-0.810802000	1.094226000
O	-3.377873000	0.861356000	-0.665717000
S	-2.410670000	0.490885000	0.424346000

$[Hg^{II}(HSO_3)]^+$
Electronic Energy = -777.8360001
Electronic and Zero-Point Energy = -777.8133731
Enthalpy = -777.8061771
Free Energy = -777.8462531

Hg	-1.585887000	0.715753000	-1.375995000
O	-3.443984000	1.695721000	1.272345000
O	-2.924559000	-0.693403000	1.341899000
O	-4.691955000	0.106497000	-0.269010000
S	-3.411180000	0.530598000	0.355655000
H	-3.097916000	-1.553033000	0.913178000

$(HSO_4)Hg^{II}(HSO_3)$
Electronic Energy = -1477.724926
Electronic and Zero-Point Energy = -1477.674015
Enthalpy = -1477.660652
Free Energy = -1477.716082

Hg	0.411547000	-0.077417000	-0.484526000
O	-2.280046000	1.089681000	1.345195000
O	3.637892000	-0.476727000	-1.266499000
O	3.002932000	-1.773923000	0.820713000
O	3.340922000	0.727249000	0.835953000
O	-2.890290000	-1.160488000	0.682354000
O	-4.024638000	0.763999000	-0.464913000
O	-1.662703000	0.301342000	-0.948860000
S	2.814422000	-0.570984000	-0.034183000
S	-2.742078000	0.369198000	0.146174000
H	3.007834000	0.671463000	1.750875000
H	-3.338549000	-1.711206000	0.014566000

TS3
Electronic Energy = -2178.011357
Electronic and Zero-Point Energy = -2177.924551
Enthalpy = -2177.905116
Free Energy = -2177.974925

Hg	0.555763000	0.739077000	0.092148000
O	-2.471483000	-0.657426000	0.803727000
O	4.027830000	0.965831000	0.056877000
O	3.270072000	-1.291705000	0.919579000
O	3.102195000	0.788979000	2.416662000
O	-2.517332000	-0.881106000	-1.611802000
O	-3.886743000	0.941650000	-0.567141000
O	-1.444414000	1.144969000	-0.597196000
S	2.983244000	0.132785000	0.673741000
S	-2.631486000	0.187490000	-0.392102000
H	2.591581000	0.254036000	3.055205000
H	-2.758920000	-0.456172000	-2.455217000
H	2.825855000	1.827521000	2.502625000
O	2.492016000	3.175570000	2.559232000
S	2.472033000	3.937995000	1.245355000
O	4.030322000	4.011124000	0.772794000
H	4.532434000	4.589183000	1.375678000
O	1.850729000	3.154450000	0.147881000
O	1.989834000	5.319396000	1.433527000

SO_2
Electronic Energy = -548.6197475
Electronic and Zero-Point Energy = -548.6130845
Enthalpy = -548.6090435
Free Energy = -548.6380105

S	-0.432872000	2.249324000	0.055513000
O	-0.501401000	0.889489000	0.621841000
O	-0.227645000	2.325304000	-1.402797000

$[(HSO_4)Hg^{II}(OH_2)]^+$
Electronic Energy = -929.5376764
Electronic and Zero-Point Energy = -929.4844664
Enthalpy = -929.4742594
Free Energy = -929.5211424

Hg	0.437671000	0.038093000	0.003176000
O	-2.510322000	1.678326000	1.002067000
O	2.551161000	0.039460000	0.515862000
O	-2.872396000	-0.675741000	1.464490000

O	-4.036784000	0.342048000	-0.516620000
O	-1.618421000	-0.026257000	-0.611707000
S	-2.794956000	0.430555000	0.273582000
H	2.815058000	0.961397000	0.666935000
H	-3.143075000	-1.539333000	1.101752000
H	2.645305000	-0.399011000	1.376925000

$Tl^{I}(HSO_4)$
Electronic Energy = -872.3532973
Electronic and Zero-Point Energy = -872.3267843
Enthalpy = -872.3184313
Free Energy = -872.3629803

Tl	-0.161769000	1.801429000	-0.524728000
O	-0.577627000	-0.282615000	1.417736000
O	-1.337177000	0.267073000	3.752490000
O	-1.864635000	1.796031000	1.848224000
O	-2.936498000	-0.472624000	1.970777000
S	-1.577606000	0.396208000	2.292837000
H	-3.645260000	-0.200781000	2.579661000

$[Tl^{III}(HSO_3)(HSO_4)]^{+}$
Electronic Energy = -1496.518825
Electronic and Zero-Point Energy = -1496.468031
Enthalpy = -1496.454489
Free Energy = -1496.510923

Tl	0.309529000	0.235046000	0.612071000
O	-1.892170000	-0.883945000	-0.238969000
O	3.579033000	-0.080098000	0.887384000
O	2.340203000	-2.342002000	1.070344000
O	2.406588000	-0.658851000	2.963133000
O	-2.472390000	0.620271000	-2.078626000
O	-3.790466000	0.816273000	0.037479000
O	-1.376007000	1.477139000	0.014895000
S	2.520601000	-0.934067000	1.406179000
S	-2.466446000	0.470274000	-0.481446000
H	1.878023000	-1.349044000	3.425565000
H	-3.121148000	1.294772000	-2.361200000

$Tl^{III}(HSO_3)(HSO_4)_2$
Electronic Energy = -2196.416333
Electronic and Zero-Point Energy = -2196.337421
Enthalpy = -2196.317691
Free Energy = -2196.388489

Tl	0.438833000	0.344972000	0.540854000
O	-1.879244000	-0.980549000	-0.463026000
O	3.606222000	-0.195665000	0.860107000
O	2.329101000	-2.402641000	1.213335000
O	2.393853000	-0.564115000	2.954562000
O	-2.535062000	0.727739000	-2.082243000
O	-3.758405000	0.664000000	0.097588000
O	-1.372088000	1.368179000	0.040003000
S	2.473993000	-0.955034000	1.397881000
S	-2.456892000	0.379058000	-0.514229000
H	1.826241000	-1.189187000	3.453941000
H	-3.151202000	1.469011000	-2.241964000
O	1.247567000	2.344507000	1.732921000
S	1.946679000	2.987013000	0.550960000
O	3.536926000	2.845221000	0.820420000
H	3.882398000	3.667335000	1.215863000
O	1.723319000	2.069857000	-0.631385000
O	1.653256000	4.412829000	0.347081000

TS forming $Tl^{III}(HSO_4)_3 + SO_2 + H_2O$
Electronic Energy = -2896.701956
Electronic and Zero-Point Energy = -2896.587098
Enthalpy = -2896.562072
Free Energy = -2896.641859

Tl	-0.006953000	-0.033944000	0.648970000
O	-1.885302000	-0.791578000	-0.267507000
O	3.436822000	-0.304083000	0.724671000
O	2.520836000	-2.596438000	1.372343000
O	2.530784000	-0.680489000	3.053464000
O	-2.323082000	0.565323000	-2.251282000
O	-3.997957000	0.610944000	-0.392251000
O	-1.684288000	1.607246000	-0.054611000
S	2.374205000	-1.134903000	1.309624000
S	-2.562010000	0.541084000	-0.662596000
H	2.079994000	-1.313605000	3.651121000
H	-3.043251000	1.050318000	-2.700576000
O	0.887927000	0.146724000	-1.516912000
S	1.599025000	1.491861000	-1.346971000
O	0.700532000	2.579988000	-2.123581000
H	1.032675000	2.716692000	-3.031549000
O	1.403017000	1.870419000	0.105053000
O	2.961733000	1.535338000	-1.885342000
H	2.211451000	0.375867000	3.248567000
O	1.825025000	1.625564000	3.269711000
S	0.336187000	1.887474000	3.383338000

O	-0.432735000	0.747823000	2.724223000
O	-0.139060000	2.192127000	4.731137000
O	0.033528000	3.106218000	2.394299000
H	0.265891000	3.965004000	2.799880000

$Tl^{III}(HSO_4)_3$
Electronic Energy = -2271.637218
Electronic and Zero-Point Energy = -2271.554169
Enthalpy = -2271.533897
Free Energy = -2271.605218

Tl	-0.317984000	0.693202000	1.005140000
O	-1.181631000	-0.149058000	-0.979307000
O	-1.287908000	1.788245000	-2.466853000
O	-3.450278000	0.801209000	-1.683366000
O	-1.904061000	1.945812000	-0.036137000
S	-2.069050000	1.052770000	-1.276878000
H	-1.909196000	2.267721000	-3.049714000
O	0.780300000	2.525572000	1.739699000
S	1.780602000	2.681892000	0.577163000
O	3.177138000	2.097475000	1.112737000
H	3.736359000	2.809701000	1.479815000
O	1.348538000	1.647859000	-0.438442000
O	1.972073000	4.063513000	0.135458000
O	1.555673000	-0.715481000	1.697259000
S	0.710774000	-1.443299000	2.715986000
O	1.187476000	-1.535554000	4.090151000
H	0.252017000	-3.017325000	1.310313000
O	0.528281000	-2.959462000	2.246984000
O	-0.694100000	-0.780709000	2.574105000

TS C-H Activation for $Tl^{III}(HSO_4)_3$
Electronic Energy = -2312.115857
Electronic and Zero-Point Energy = -2311.990764
Enthalpy = -2312.262901
Free Energy = -2312.042333

Tl	0.639970000	0.691167000	1.419920000
O	-0.814564000	-0.596246000	-0.466203000
O	-1.130749000	1.174967000	-2.110167000
O	-3.071954000	0.552220000	-0.645722000
O	-1.076171000	1.694997000	0.342023000
S	-1.608358000	0.662042000	-0.662045000
H	-1.775218000	1.808784000	-2.480734000
O	1.345503000	2.807423000	1.563621000
S	1.808706000	3.137037000	0.123231000

O	3.374050000	3.490793000	0.259655000
H	3.494596000	4.449850000	0.396614000
O	1.786698000	1.857278000	-0.642001000
O	1.116042000	4.306918000	-0.431768000
H	1.093068000	-1.510107000	1.860742000
C	2.188713000	-0.935859000	1.535717000
H	2.616961000	-0.525891000	0.605074000
H	2.800359000	-0.736212000	2.417782000
H	2.223562000	-2.015265000	1.246740000
O	0.024806000	-2.365849000	2.340985000
S	-1.315219000	-1.727252000	2.625224000
O	-2.018127000	-2.226582000	3.804814000
H	-1.837776000	-1.828905000	0.549023000
O	-2.269472000	-2.107541000	1.391323000
O	-1.153958000	-0.212309000	2.601342000

$(HSO_4)_2Tl^{III}(CH_3)$
Electronic Energy = -1611.880587
Electronic and Zero-Point Energy = -1611.789866
Enthalpy = -1611.988216
Free Energy = -1611.836554

Tl	0.942158000	0.328521000	1.054317000
O	-0.549070000	-0.387323000	-1.335329000
O	-1.204517000	1.900232000	-1.891130000
O	-2.928105000	0.402598000	-0.877697000
O	-1.013098000	1.181397000	0.502172000
S	-1.481344000	0.668325000	-0.880706000
H	-1.944938000	2.535086000	-1.858786000
O	1.358618000	2.757180000	1.424758000
S	1.667156000	3.118464000	-0.010288000
O	3.215002000	3.605680000	-0.047862000
H	3.277923000	4.545098000	0.205415000
O	1.711069000	1.844073000	-0.808881000
O	0.842781000	4.210684000	-0.558041000
C	2.347215000	-1.085226000	1.831267000
H	2.957954000	-1.357512000	0.964761000
H	2.892312000	-0.532857000	2.602604000
H	1.737094000	-1.905420000	2.220115000

$(HSO_4)Tl^{III}(CH_3)$
Electronic Energy = -911.9878496
Electronic and Zero-Point Energy = -911.9248936
Enthalpy = -911.9143016
Free Energy = -911.9643196

Tl	-0.443019000	-0.352144000	0.014997000
C	-2.571264000	-0.302597000	0.063864000
H	-2.843997000	-0.061027000	-0.968174000
H	-2.846065000	-1.311741000	0.385809000
H	-2.795394000	0.484900000	0.790151000
O	1.293510000	1.667128000	0.764470000
S	2.382916000	0.733333000	0.376200000
O	3.459171000	0.433857000	1.318417000
O	3.143211000	1.313356000	-0.914698000
O	1.681396000	-0.568754000	-0.131666000
H	2.509339000	1.631341000	-1.586743000

TS functionalization of $(HSO_4)_2Tl^{III}(CH_3)$
Electronic Energy = -1611.857424
Electronic and Zero-Point Energy = -1611.767246
Enthalpy = 1611.964164
Free Energy = -1611.815855

Tl	-0.505129000	-0.310308000	-0.099487000
C	-2.803234000	-0.291511000	0.086491000
H	-3.024040000	-0.511632000	-0.959174000
H	-2.882951000	-1.099159000	0.816447000
H	-2.889297000	0.737868000	0.439995000
S	-5.798706000	0.938229000	-0.252698000
O	-5.221804000	-0.328587000	0.309926000
O	-5.115645000	1.419737000	-1.477543000
O	-5.393915000	2.114428000	0.827939000
O	-7.283905000	0.915012000	-0.311393000
H	-5.797800000	1.911795000	1.689639000
O	1.282131000	1.507105000	0.852800000
S	2.398023000	0.648401000	0.354367000
O	3.471684000	0.292116000	1.287730000
O	3.169465000	1.449582000	-0.818410000
O	1.757804000	-0.569638000	-0.334573000
H	2.532925000	1.845654000	-1.443095000

$Cd^{II}(HSO_4)_2$
Electronic Energy = -1567.317536
Electronic and Zero-Point Energy = -1567.262448
Enthalpy = -1567.248073
Free Energy = -1567.307008

Cd	0.088146000	0.582410000	0.971456000
S	-3.059063000	-0.440171000	0.444039000
S	3.297869000	-0.004254000	0.095731000
O	-2.092500000	0.573709000	1.037254000

O	-4.295802000	-0.512795000	1.252503000
O	-3.470587000	0.174664000	-1.012205000
O	2.685370000	-0.235031000	-1.403287000
O	4.550268000	0.768893000	-0.048721000
O	2.250240000	0.822418000	0.826413000
O	3.413455000	-1.383261000	0.609887000
O	-2.403279000	-1.713098000	0.082273000
H	-4.015832000	0.973052000	-0.893436000
H	2.685746000	0.606487000	-1.893806000

TS C-H activation for $Cd^{II}(HSO_4)_2$
Electronic Energy = -1607.754779
Electronic and Zero-Point Energy = -1607.657932
Enthalpy = -1607.641076
Free Energy = -1607.705836

Cd	0.661123000	-1.319086000	-0.652194000
S	-3.095369000	0.798598000	-0.984271000
S	3.936772000	-0.517817000	-0.651389000
O	-3.409103000	2.168598000	-1.420571000
O	-4.001625000	0.179686000	0.001491000
O	-3.063207000	-0.172186000	-2.290395000
O	4.177089000	-1.304885000	0.765374000
O	3.568496000	0.876354000	-0.309705000
O	5.166398000	-0.677411000	-1.458285000
O	2.790370000	-1.329279000	-1.214601000
O	-1.614589000	0.699980000	-0.572448000
C	-1.236612000	-1.688003000	0.452830000
H	-1.288846000	-0.383641000	-0.181615000
H	-0.662528000	-2.556870000	0.826148000
H	-1.569111000	-1.171490000	1.365916000
H	-2.092464000	-2.104562000	-0.097774000
H	-3.972452000	-0.372396000	-2.580365000
H	4.849869000	-0.836834000	1.291605000

$(HSO_4)Cd^{II}(CH_3)$
Electronic Energy = -907.4692624
Electronic and Zero-Point Energy = -907.4076514
Enthalpy = -907.3968784
Free Energy = -907.4452734

Cd	1.044030000	-0.184468000	-0.050066000
O	-1.050697000	-0.559264000	0.498483000
O	-2.622528000	1.070166000	1.332247000
O	-1.909091000	1.175287000	-1.077252000
O	-3.413519000	-0.668998000	-0.287086000

S	-2.253112000	0.206581000	-0.008430000
H	-3.473684000	1.525636000	1.204069000
C	3.137466000	-0.143710000	-0.400259000
H	3.665453000	-0.299352000	0.552430000
H	3.409252000	-0.947208000	-1.100465000
H	3.435529000	0.826116000	-0.824214000

TS functionalization of $(HSO_4)Cd^{II}(CH_3)$
Electronic Energy = -907.4001138
Electronic and Zero-Point Energy = -907.3370718
Enthalpy = -907.3272008
Free Energy = -907.3738128

Cd	-0.116982000	-0.236096000	-0.051667000
C	-2.802514000	-0.205250000	0.056889000
H	-2.721198000	-0.194637000	-1.027748000
H	-2.698093000	-1.150260000	0.585228000
H	-2.665966000	0.720049000	0.615320000
S	-5.399772000	1.028049000	-0.243615000
O	-4.688819000	-0.279887000	0.125922000
O	-4.774800000	1.716571000	-1.387985000
O	-5.074244000	2.039743000	0.994938000
O	-6.860821000	0.813340000	-0.277666000
H	-5.525279000	1.729468000	1.801126000

$Zn^{II}(HSO_4)_2$
Electronic Energy = -3178.881085
Electronic and Zero-Point Energy = -3178.825302
Enthalpy = -3178.81139
Free Energy = -3178.867643

Zn	-0.048717000	-0.323533000	-0.632765000
S	-3.109988000	0.358603000	0.005479000
S	3.116651000	-0.022257000	-0.395706000
O	-1.952454000	-0.066838000	-0.898663000
O	-4.287116000	0.679527000	-0.825767000
O	-3.472435000	-0.973672000	0.870491000
O	3.237470000	1.232705000	0.636164000
O	4.203025000	-0.967336000	-0.070666000
O	1.768540000	-0.660255000	-0.064010000
O	3.138653000	0.631556000	-1.715853000
O	-2.709065000	1.326523000	1.041934000
H	-3.885220000	-1.642546000	0.294290000
H	3.340613000	0.902463000	1.547473000

TS C-H activation for $Zn^{II}(HSO_4)_2$

Electronic Energy = -3219.318706
Electronic and Zero-Point Energy = -3219.220703
Enthalpy = -3219.204503
Free Energy = -3219.265142

Zn	0.939628000	-1.990157000	-0.226134000
S	-0.517669000	1.577934000	-0.919713000
S	3.829857000	-0.948808000	-0.694757000
O	-0.478603000	2.612871000	-1.967149000
O	0.403793000	1.696954000	0.223334000
O	-1.983644000	1.623580000	-0.212317000
O	4.290738000	-0.778857000	0.860609000
O	3.164125000	0.307279000	-1.103392000
O	5.017829000	-1.355274000	-1.469749000
O	2.848009000	-2.107411000	-0.542087000
O	-0.452782000	0.179433000	-1.558795000
C	-0.980496000	-1.622179000	0.288906000
H	-0.556062000	-0.737924000	-0.705196000
H	-0.865930000	-2.648500000	0.693347000
H	-1.115290000	-0.948241000	1.145125000
H	-1.903149000	-1.691999000	-0.306182000
H	-2.682224000	1.645236000	-0.892036000
H	4.938211000	-0.054717000	0.938659000

$(HSO_4)Zn^{II}(CH_3)$
Electronic Energy = -2519.030448
Electronic and Zero-Point Energy = -2518.967683
Enthalpy = -2518.957574
Free Energy = -2519.002852

Zn	0.987069000	0.466800000	-0.008958000
S	-2.069864000	0.839663000	0.467192000
O	-1.619120000	1.634929000	1.625230000
O	-3.190288000	-0.101018000	0.672387000
O	-2.578088000	1.977971000	-0.582394000
O	-0.917666000	0.143805000	-0.254330000
C	2.848541000	0.903486000	0.240330000
H	3.410775000	0.026522000	0.594189000
H	2.941452000	1.711320000	0.982715000
H	3.282101000	1.247126000	-0.711501000
H	-2.938089000	1.552765000	-1.381606000

TS functionalization of $(HSO_4)Zn^{II}(CH_3)$
Electronic Energy = -2518.936987
Electronic and Zero-Point Energy = -2518.873626
Enthalpy = -2518.863958

Free Energy = -2518.908996

Zn	-0.245596000	-0.201510000	0.025397000
C	-2.816863000	-0.202554000	0.039657000
H	-2.706619000	-0.203402000	-1.043006000
H	-2.691166000	-1.139543000	0.577395000
H	-2.672207000	0.727830000	0.587398000
S	-5.388143000	1.024091000	-0.245377000
O	-4.666976000	-0.287771000	0.102969000
O	-4.786750000	1.715079000	-1.399818000
O	-5.035212000	2.028200000	0.989723000
O	-6.847782000	0.802923000	-0.247809000
H	-5.471171000	1.717749000	1.804214000

TS C-H activation transition state for CH_3OSO_3H
Electronic Energy = -2292.488458
Electronic and Zero-Point Energy = -2292.37113
Enthalpy = -2292.349719
Free Energy = -2292.423452

Hg	0.912109000	-2.460580000	-0.372600000
O	-0.547085000	0.486315000	-0.634470000
O	2.910674000	-3.176096000	-0.704948000
O	5.359747000	-3.169330000	-0.454747000
O	4.011175000	-1.287294000	0.536498000
O	3.828521000	-3.589089000	1.498318000
O	-0.814694000	1.587304000	1.502730000
O	1.402712000	0.561108000	0.915498000
O	0.631473000	2.644843000	-0.259394000
S	4.095925000	-2.711335000	0.150340000
S	0.285164000	1.333164000	0.322503000
H	4.367807000	-3.242349000	2.232515000
H	-0.414202000	2.111436000	2.219414000
C	-1.236612000	-1.908433000	0.130894000
H	-2.085609000	-1.533067000	-0.467531000
H	-1.348535000	-3.006821000	0.085716000
H	-0.622246000	-0.857490000	-0.396759000
O	-1.285049000	-1.465995000	1.500413000
S	-2.711863000	-0.964397000	2.062228000
O	-3.398678000	-0.164984000	1.046549000
O	-2.417784000	-0.457180000	3.394692000
O	-3.506308000	-2.346819000	2.254660000
H	-4.131545000	-2.492912000	1.518319000

$[O_3SOOSO_3]^{2-}$
Electronic Energy = -1398.416973

Electronic and Zero-Point Energy = -1398.384155
Enthalpy = -1398.373773
Free Energy = -1398.421021

O	0.476701000	-0.502915000	-0.738375000
O	-0.475415000	0.545936000	-0.705524000
S	1.903597000	0.033806000	0.063541000
S	-1.903776000	-0.037413000	0.061462000
O	1.510244000	0.300891000	1.466233000
O	2.321963000	1.238060000	-0.695128000
O	2.715060000	-1.186466000	-0.162319000
O	-2.324681000	-1.191850000	-0.769722000
O	-2.711407000	1.196781000	-0.090353000
O	-1.512108000	-0.393223000	1.445183000

$[SO_4]^{\bullet-}$
Electronic Energy = -699.1821107
Electronic and Zero-Point Energy = -699.1687147
Enthalpy = -699.1631027
Free Energy = -699.1972937

S	-0.086902000	0.000012000	-0.001508000
O	-0.892498000	1.245050000	0.000695000
O	0.979563000	-0.000179000	-1.121621000
O	0.979388000	0.000068000	1.123024000
O	-0.892649000	-1.244963000	0.000918000

$H_2S_2O_8$
Electronic Energy = -1399.246257
Electronic and Zero-Point Energy = -1399.190382
Enthalpy = -1399.179021
Free Energy = -1399.227284

O	1.794825000	-1.421298000	2.012627000
O	0.843077000	-1.064756000	2.998187000
S	1.559175000	-0.361568000	0.706809000
S	1.734369000	-0.571772000	4.360690000
O	2.007207000	0.964325000	1.093554000
O	0.221430000	-0.610899000	0.189406000
O	2.695660000	-1.029260000	-0.167828000
O	2.557844000	-1.703470000	4.761251000
O	0.450089000	-0.387507000	5.263615000
O	2.294451000	0.743726000	4.107647000
H	2.371642000	-1.813806000	-0.659485000
H	0.153078000	-1.232950000	5.662727000

TS4
Electronic Energy = -739.6610578
Electronic and Zero-Point Energy = -739.6071548
Enthalpy = -739.5988738
Free Energy = -739.6396098

S	-0.901481000	0.961637000	0.056033000
O	-1.771305000	1.881236000	0.844195000
O	-0.986938000	1.155154000	-1.423722000
O	0.643946000	1.429750000	0.305285000
O	-1.001175000	-0.458938000	0.499203000
C	0.946966000	0.981646000	2.798780000
H	0.901356000	1.249802000	1.593981000
H	1.794939000	1.579435000	3.151909000
H	1.113497000	-0.100869000	2.822252000
H	-0.025412000	1.298540000	3.191422000

CH_3SO_3•
Electronic Energy = -663.6662291
Electronic and Zero-Point Energy = -663.6190341
Enthalpy = -663.6123061
Free Energy = -663.6486071

S	0.076358000	0.089984000	-0.000056000
O	0.286393000	1.543223000	-0.001579000
O	0.764320000	-0.681460000	1.132494000
O	0.762052000	-0.684151000	-1.132177000
C	-1.641077000	-0.296174000	0.001245000
H	-2.071744000	0.153402000	0.905119000
H	-2.071820000	0.151429000	-0.903657000
H	-1.733831000	-1.388428000	0.002063000

CH_3OSO_2•
Electronic Energy = -663.684825
Electronic and Zero-Point Energy = -663.635766
Enthalpy = -663.62894
Free Energy = -663.666268

S	0.833899000	0.962651000	0.135471000
O	-0.118445000	2.141048000	0.761128000
O	2.109439000	1.074954000	0.888435000
O	0.829016000	1.053230000	-1.352272000
C	-1.304765000	2.480741000	0.007543000
H	-1.807280000	3.235585000	0.620977000
H	-1.026207000	2.896108000	-0.968216000
H	-1.957627000	1.605645000	-0.107399000

TS5
Electronic Energy = -704.1546475
Electronic and Zero-Point Energy = -704.0661355
Enthalpy = -704.0568295
Free Energy = -704.0993015

S	-0.067282000	2.159194000	-0.002847000
O	1.260547000	2.581139000	0.794627000
O	-0.281112000	0.768429000	0.465510000
O	0.102136000	2.397246000	-1.448895000
C	-1.329224000	3.222519000	0.631745000
H	-1.365432000	3.087711000	1.718702000
H	-1.069368000	4.252211000	0.356569000
H	-2.270848000	2.917273000	0.158363000
C	1.843382000	4.966847000	-0.096116000
H	2.924164000	4.991678000	-0.278835000
H	1.509732000	5.628276000	0.711115000
H	1.239004000	5.026963000	-1.007921000
H	1.680295000	3.862495000	0.339145000

TS forming $CH_3OSO_2H + CH_3^{\bullet}$
Electronic Energy = -704.142342
Electronic and Zero-Point Energy = -704.054371
Enthalpy = -704.044683
Free Energy = -704.088649

S	-1.109573000	2.546696000	-0.820436000
O	-0.884874000	3.720796000	0.235084000
O	-0.145147000	1.345116000	-0.184519000
O	-0.386601000	2.855302000	-2.090491000
C	-0.440455000	0.993394000	1.175685000
H	-0.014630000	-0.003822000	1.331655000
H	0.023040000	1.712156000	1.865706000
H	-1.525984000	0.949797000	1.353466000
C	1.641074000	4.135057000	0.336985000
H	1.802659000	4.342478000	1.401164000
H	1.810891000	4.982333000	-0.335937000
H	2.052790000	3.183069000	-0.011928000
H	0.384714000	4.008909000	0.307755000

CH_3SO_3H
Electronic Energy = -664.3600803
Electronic and Zero-Point Energy = -664.2997363
Enthalpy = -664.2928693
Free Energy = -664.3287743

S	-0.079673000	2.176415000	0.009695000
O	1.236763000	2.685428000	0.815435000
O	-0.277768000	0.791884000	0.471190000
O	0.125574000	2.436130000	-1.428900000
C	-1.364035000	3.217516000	0.635867000
H	-1.409995000	3.074825000	1.721690000
H	-1.116828000	4.252263000	0.370243000
H	-2.294561000	2.895640000	0.151470000
H	1.650731000	3.433859000	0.346022000

CH_3OSO_2H
Electronic Energy = -664.3375754
Electronic and Zero-Point Energy = -664.2773784
Enthalpy = -664.2700674
Free Energy = -664.3074604

S	0.731797000	0.934560000	0.116793000
O	-0.018621000	2.347709000	0.590034000
O	2.128490000	1.284103000	0.915875000
O	1.112376000	1.125933000	-1.310774000
C	-1.326301000	2.500498000	0.012859000
H	-1.790045000	3.344393000	0.534457000
H	-1.253200000	2.723901000	-1.060790000
H	-1.940497000	1.600627000	0.172833000
H	2.105903000	0.925514000	1.822594000

TS HAT $CH_3SO_3\bullet$ and CH_3OSO_3H
Electronic Energy = -1403.23734
Electronic and Zero-Point Energy = -1403.126314
Enthalpy = -1403.112461
Free Energy = -1403.167642

S	0.237160000	1.629505000	-0.252197000
O	0.437638000	3.183645000	0.066744000
O	1.185367000	1.189423000	-1.294621000
O	-1.216355000	1.547713000	-0.536153000
C	0.616591000	0.817153000	1.271748000
H	1.667102000	1.033313000	1.506809000
H	-0.059674000	1.212648000	2.038203000
H	0.462413000	-0.257599000	1.114813000
C	3.043546000	3.541928000	0.279025000
H	3.274885000	3.721592000	1.334980000
H	3.428753000	2.593771000	-0.124740000
H	1.855394000	3.459563000	0.237450000
S	3.450279000	4.542176000	-2.078500000

O	3.833191000	5.872720000	-2.528990000
O	4.621352000	3.487051000	-2.329432000
O	2.230206000	3.870306000	-2.502750000
H	5.502860000	3.900805000	-2.229598000
O	3.443868000	4.672732000	-0.443719000

Explicitly solvated ground-state structures.

Figure S1 shows the six lowest free energy structures for $Hg(HSO_4)_2(H_2SO_4)$. These structures are within 3 kcal/mol of the lowest energy structure. All of these structures feature hydrogen bonding between sulfuric acid solvent and the bisulfate ligands. No low-energy structures have H_2SO_4 hydrogen bonding to the Hg metal center or solvent H_2SO_4 coordinating to the Hg metal center for an expanded valence coordination.

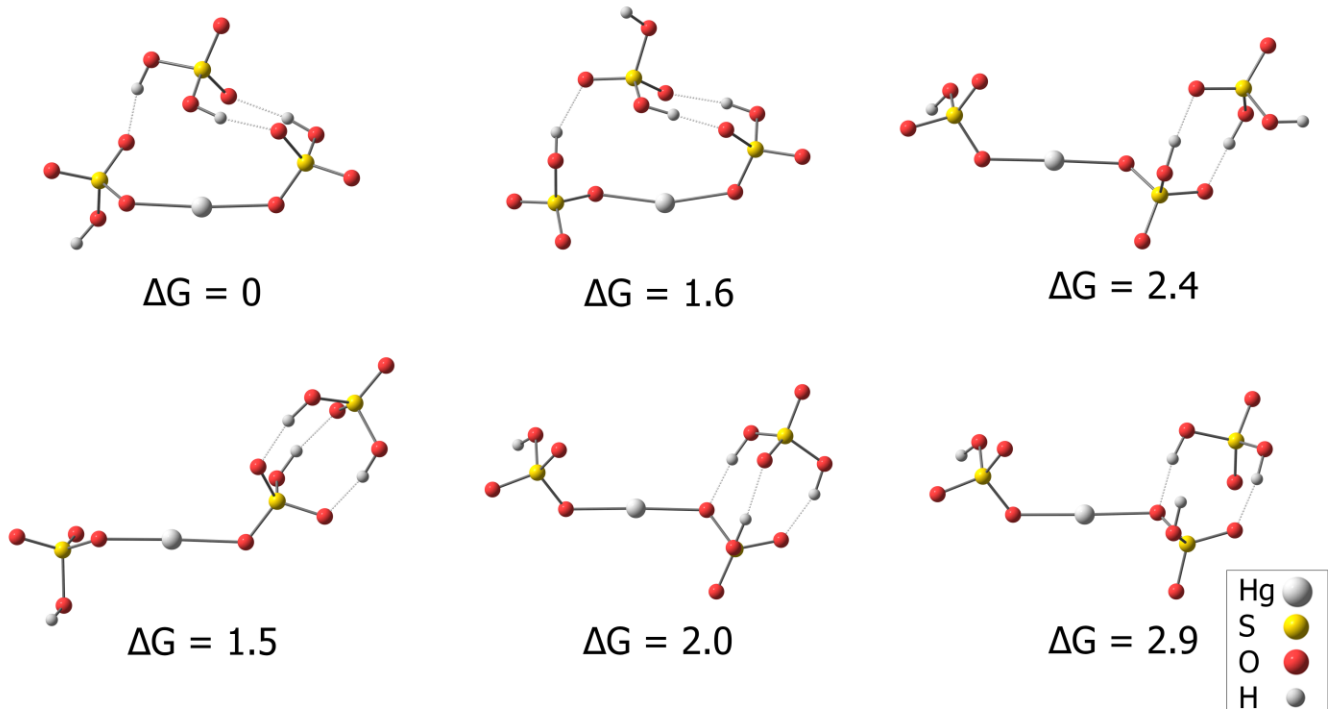


Figure S1. Ground-state conformations and relative free energies for $Hg(HSO_4)_2$ with one explicit H_2SO_4 solvent and implicit solvent. (kcal/mol)

Free energy landscape with explicit solvent.

Figure S2 is the free energy surface for C-H activation and MR functionalization with explicit solvent. The energies of this free energy surface are very similar to the energy surface without explicit solvation.

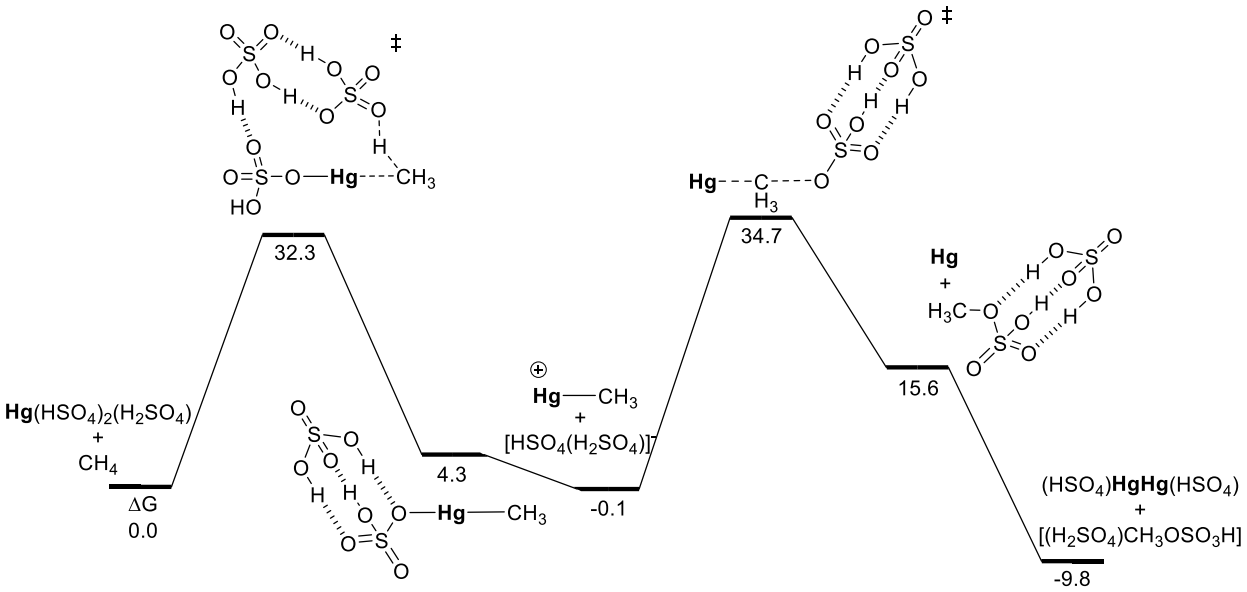
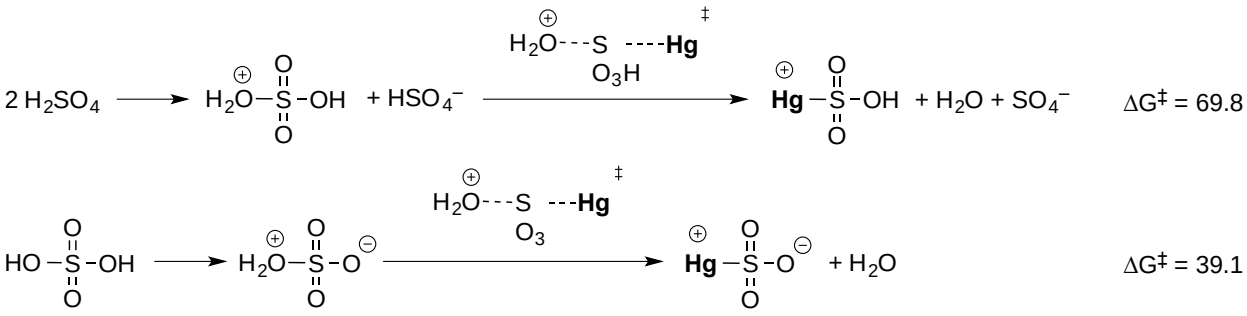


Figure S2. Free energy surface for C-H activation and MR functionalization with explicit H_2SO_4 solvation. (kcal/mol)

Alternative Hg oxidation pathways.



Tl^{III} C-H activation and MR functionalization.

Figure S3 plots the free energy surface for methane C-H activation and MR functionalization by $Tl(HSO_4)_3$.

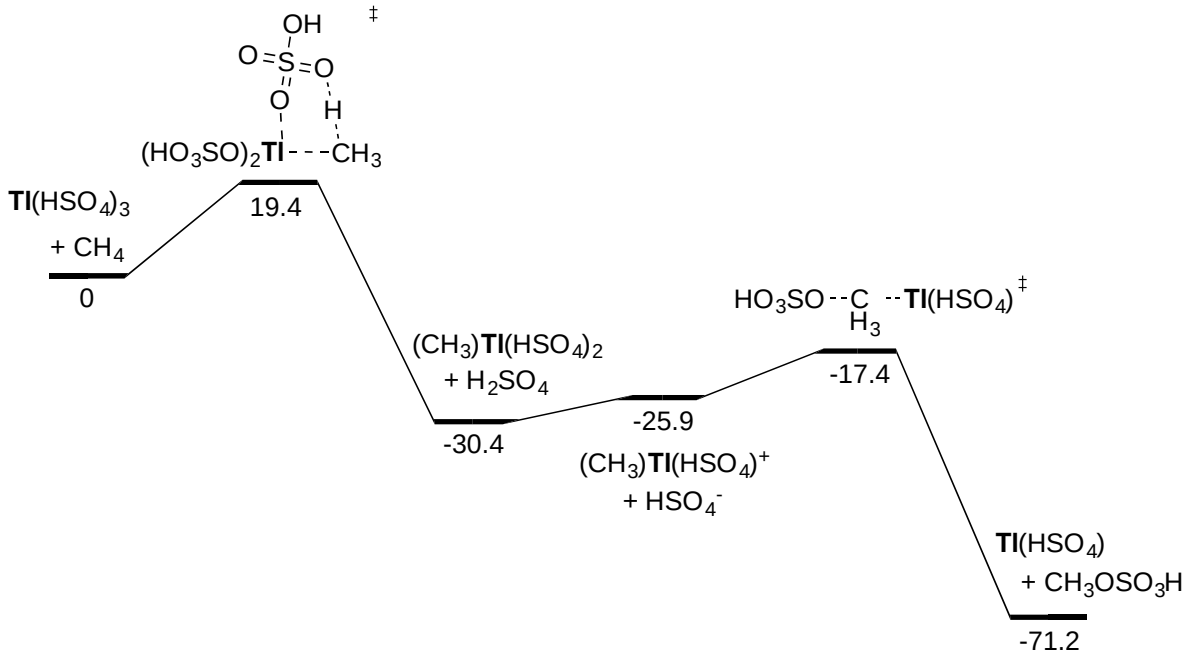


Figure S3. Tl^{III} C-H activation and Tl-CH3 functionalization free energy surface. (kcal/mol)

Dinuclear Hg transition states.

The transition states shown below were the lowest energy C-H activation and MR functionalization transition states identified using a binuclear Hg catalyst structure (free energies in kcal/mol). These calculations suggest that C-H activation from a dinuclear Hg species is unlikely. We did locate a MR functionalization transition state with a dinuclear Hg model that is lower in energy than the MR functionalization presented in the main text. However, there are several things to note about this transition state. It is not clear how this transition state is connected to the energy surface with a single Hg metal center. This MR functionalization barrier, if lower than the barrier for C-H activation, does not fit with the experimental observation of H/D exchange during catalysis in D_2SO_4. There is the possibility, however, that H/D exchange

occurs through a concerted protonation-deprotonation transition state between methane and D_2SO_4. This transition state has an activation enthalpy of 34.4 kcal/mol and this is several kcal/mol higher than the Hg-promoted activation enthalpy for **TS1b** of 23.7 kcal/mol.